THERMOELECTRIC

BONDING STUDY

PHASE III -

SUMMARY REPORT

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By

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FOREWORD

This report covers the work performed during Phase III of the Thermo-electric Bonding Study performed for the National Aeronautics and Space Administration under Contract NAS5-3973. Mr. Joseph Epstein is technical officer for NASA-GSFC.

I. INTRODUCTION

The National Aeronautics and Space Administration has a continuing interest in the development of thermoelectric power supplies for space systems. Such power supplies when fueled with radioisotope heat sources offer promise of reliable, long term operation and are particularly attractive at power levels of a few watts to one kilowatt or more.

Lead telluride, because of its high efficiency in the 500° to 1100°F range, is most often considered as the thermoelectric converter material in radioisotope thermoelectric generators (RTGs). However, the performance of lead telluride RTGs built to date has been disappointing. Declines in power output are typically observed early in life due to increases in internal resistance in the generator, particularly at the junctions between the thermoelectric elements and the metal contacts to which they are joined.

Hittman Associates, under Contract NAS5-3973, has been studying the bonding of lead telluride to electrical contact materials with the primary objective of determining the operative degradation mechanism in bonded thermoelectric elements. During the first phases of this program it was found that two independent mechanisms were responsible for the observed effect.

(1) Diffusion of material from the braze or electrical contact into the thermoelectric causing poisoning and an attendant decline in performance.

(2) Cracking of the lead telluride due to stresses generated during the bonding process. Such stresses are related to the mismatch in thermal expansion between lead telluride and the commonly used electrical contact materials such as iron.

It was also demonstrated that p-type lead telluride is highly susceptible to failure while the n-type material is quite resistant.

In succeeding phases of this program the bonding of lead telluride to iron contacts (shoes) with a modified tin telluride braze was studied in detail. Long term life tests, at hot junction temperature of 950° - 1000°F have been carried out to study the pattern of degradation. The use of additives to strengthen p-PbTe and stainless steel shoes which closely match the thermal expansion of lead telluride and may therefore minimize stresses have also been investigated.

This work has been continued and expanded during the current phase. The accomplishments during the six month period covered by this report are described in the succeeding chapters.

II. SUMMARY AND CONCLUSIONS

During the current contract period, work has been carried forward in three areas of the lead telluride bonding study. The majority of the effort was concentrated on life tests of braze bonded lead telluride elements with less emphasis on studies of the effects of additives on the strength and performance of p-PbTe and the possible advantages of using austenitic stainless steel shoes for p-PbTe.

Tests of twenty-one n-PbTe and thirty-three p-PbTe elements bonded to iron shoes with SnTe-Ti braze have now been completed, the longest runs being 5900 hours for the n-type material and 3570 hours for p-PbTe. Hot junction temperature was held at 950° - 1000°F during these runs. Currently operating tests have now exceeded 4000 hours and 5700 hours each for six n- and six p-type elements respectively. Typically, the power output of n-PbTe elements increases during the first several hundred hours and then levels off and remains constant for the remainder of the period of operation. Measurements made on elements removed from test showed no significant changes in bond resistance, resistivity or Seebeck coefficient from pre-test values.

The time versus power curve of p-PbTe is considerably different. Most often a sharp initial decline has been observed over the first 500 - 600 hours of test followed by a continual decline at a lower rate that is constant or slightly decreasing. During this period the degradation rate is about five to ten percent per 1000 hours. In several elements a leveling off of power output has been observed after 2000 to 3000 hours of operation. Post-test measurements of resistivity and Seebeck coefficient were erratic and appeared unrelated to performance. However, an increase in bond resistance from pre-test values was observed in all samples.

Electron microprobe studies were performed on a number of n- and p-type elements at GSFC. The most significant observation was that tin diffuses extensively from the braze into the lead telluride and that this diffusion is similar for both types of material. The depth to which the tin penetrates increases with test time but the rate of increased penetration decreases with time, both these observations being typical of diffusion processes.

Earlier in this program (Reference 3) it was shown that the uniform dispersion of one percent by weight of tin increases the resistivity of p-PbTe by a factor of approximately fifteen but does not affect the properties of n-PbTe. This evidence indicates that the measured increase in resistance at or near the bond in p-PbTe is caused by the diffusion of tin into the lead telluride in this region, and that the observed decline in power of p-PbTe thermoelectric elements is caused principally by this local resistance increase.

The work performed during this period substantiated our earlier results showing that small molybdenum and tungsten additions can significantly strengthen p-PbTe, with molybdenum being particularly effective. Several 1000 hours life tests demonstrated that tungsten powder or wire and molybdenum wire have no detrimental effect on the performance of p-PbTe. Excessive initial degradation was observed in elements containing the molybdenum additive in powder form. Longer tests of samples containing molybdenum wire additives confirmed that the behavior of such elements is comparable to unmodified p-PbTe.

The limited effort on bonding p-PbTe to stainless steel shoes showed that the residual stress within the thermoelectric element is indeed reduced. Such bonds appear to offer no other advantage over the customary iron shoes.

The combined work completed to date under this contract has shown that poisoning of p-type lead telluride by diffusion of material from the braze or shoe and cracking of the p-PbTe caused by stresses generated during the bonding operation are the principal mechanisms of failure in bonded lead telluride thermoelectric elements and couples. In the tin telluride-titanium brazed elements studied extensively during the most recent phases of the program, the first mechansim appears to be the operative one with diffusion of tin specifically causing a sharp rise in resistance at the braze - lead telluride interface. Based on the results obtained, one can predict the rate of power decline of lead telluride couples operated at 950° - 1000°F hot junctions and can minimize the decline by matching the load resistance to predicted end-of-life conditions rather than beginning-of-life conditions as is often done at present.

III. LIFE TESTING OF BONDED LEAD TELLURIDE

Life tests of lead telluride thermoelectric elements were initiated during the previous phase. Sample preparation and test equipment are described in detail in the summary report covering the earlier portion of this program (Reference 1) and will only be briefly described herein.

A. Preparation of Test Specimens

Most thermoelectric elements tested during the course of this program were hot pressed at Hittman Associates from lead telluride powders purchased from Minnesota Mining and Manufacturing Company (3M Company). The few exceptions were cold pressed and sintered elements purchased from 3M in the as-fabricated condition. The purchased powders were identified as TEG-2N (n-PbTe) and TEG-2P (p-PbTe).

Test elements 3/8 inch diameter by approximately 3/4 inch high were prepared by weighing out the correct quantity of powder and loading it into a graphite die. The ends of the die pins were coated with high purity alumina to prevent sticking to the compacts. The loaded die was placed inside an induction coil within an argon atmosphere pressing chamber. The chamber itself was located between the platens of a small hydraulic press. The chamber was then purged, the die was heated to the pressing temperature, load was applied for the requisite time, and the system was cooled under load. Pressing conditions for n-PbTe and p-PbTe are shown in Table I.

The elements produced by this process were uniformly sound. Densities were 97 to 100 percent of theoretical. Quality was evaluated by room temperature electrical resistivity and low temperature Seebeck coefficient measurements on all elements. For both n- and p-PbTe the measured resistivity was consistently below the values reported by 3M for elements prepared by their cold pressing and sintering process. This is presumably due to the higher densities achieved at Hittman Associates by hot pressing. Seebeck coefficient was usually below that claimed by 3M to be typical of their product. However, other laboratories using 3M elements or powders have measured similar low values for this parameter (Reference 2).

The thermoelectric elements were prepared for life testing by bonding to iron shoes with SnTe - 1 w/o Ti braze alloy. Bonding was accomplished by holding the assembly at 1500°F for five minutes in an argon atmosphere. Rapid cooling from the bonding temperature was possible for n-PbTe, but p-PbTe elements had to be cooled at slow, controlled rates to prevent cracking. Considerable success was achieved when the cooling rate was held to 50°F per hour. Details of the bonding process and equipment are described in Reference 1.

Subsequent to bonding the thermoelectric properties were remeasured and, if these were not significantly different than the values measured in the unbonded state, the element was accepted for life testing. Braided copper lead wires were attached to each iron shoe as the final assembly step. Figure 1 shows a completed element ready for testing.

TABLE I

Hot Pressing Conditions for Lead Telluride Thermoelectric Elements

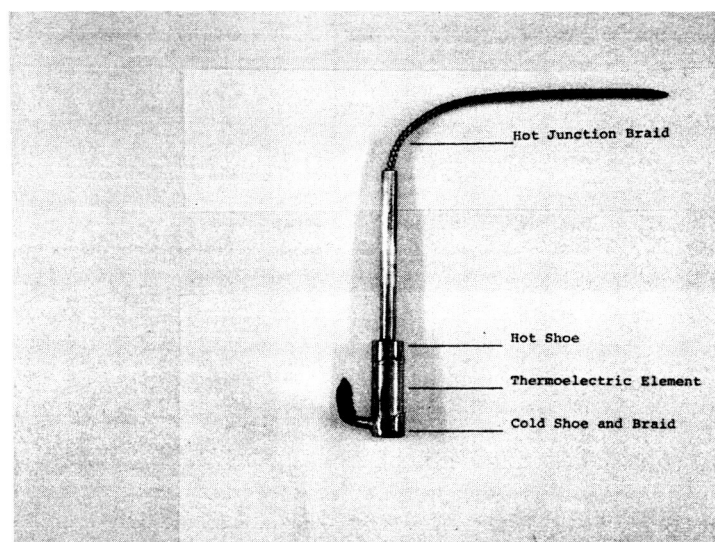|	n-PbTe	p-PbTe
Temperature	1450 - 1500°F	1500°F
Load	2500 - 3000 psi	3000 psi
Time	5 minutes	5 minutes
Atmosphere	Argon	Argon

Figure 1

Lead Telluride Thermoelectric Element for Use in Life Test Apparatus

B. Life Tests of n-PbTe

The equipment used for life testing consists of four units each of which has capacity for six individual thermoelectric elements. Measurements are made of hot junction temperature, cold junction temperature, open circuit voltage, total element resistance and power output.

During the period convered by this report two tests of n-PbTe were carried out. One group was removed from test after more than 5900 hours of operation. The second group is still on test and as of October 1, had accumulated 4000 hours of operation.

The 5900 hour test group included three Hittman Associates produced TEG-2N thermoelements bonded to iron shoes, one 3M Company produced TEGS-2N element bonded at the hot end only, and two unbonded controls, one produced at Hittman Associates and the other purchased from 3M.

Figures 2 through 4 show the performance of the bonded test elements. Over the first 2,000 hours power increased steadily due to a continual decline in resistance. At this point, a utility failure caused two thermal cycles. Immediate increases in resistance and declines in power were observed. These were largely recovered within a few hundred hours. A heater failure caused a thermal cycle and temporary shutdown of the system after 3100 hours. During attempts to remove the failed heater, which was stuck firmly in the heater block, the elements were unintentionally stressed. Upon restart this was manifested as a sharp rise in resistivity and accompanying decline in power. During the last 3000 hours of testing, the power output of elements 186 and 189 (Figure 2 and 3) slowly increased to approximately the level measured immediately prior to the failure. The output of element 197 (Figure 4) remained substantially below earlier levels.

Upon removal from the life tester all the elements appeared sound. The iron hot shoes generally displayed an oxide layer although the PbTe showed less discoloration. Figure 5 shows the appearance of a typical element. The cold shoe of element 197 separated during handling. Incipient failure of this bond apparently had caused the unrecovered power decline discussed above. The hot shoes of the two contact bond element had bonded to the elements during the extended time at temperature. The resistance of these bonds was measured along with other pertinent resistances and Seebeck coefficients and are compared to pre-test values in Table II. Changes in bond resistance, resistivity and Seebeck coefficient were small in the four bonded elements and were probably within the experimental accuracy of the test equipment. The electrical resistivity of the two unbonded thermoelectric elements showed significant changes, declining 13 and 18 percent in the two samples. The cause of this is not apparent. As was stated previously, the hot shoes adhered to these elements during the test. Contact resistances, which were 570 and 420 $\mu\Omega$, were high when compared to the 40 to 80 $\mu\Omega$ measured on the braze bonded samples after testing.

The elements were mounted, polished and examined metallographically. This examination showed that extensive oxidation had occurred at the hot junction bond of all the elements. This was manifested in two ways - a heavy layer of oxide at the iron-braze interface and an oxide phase distributed througout
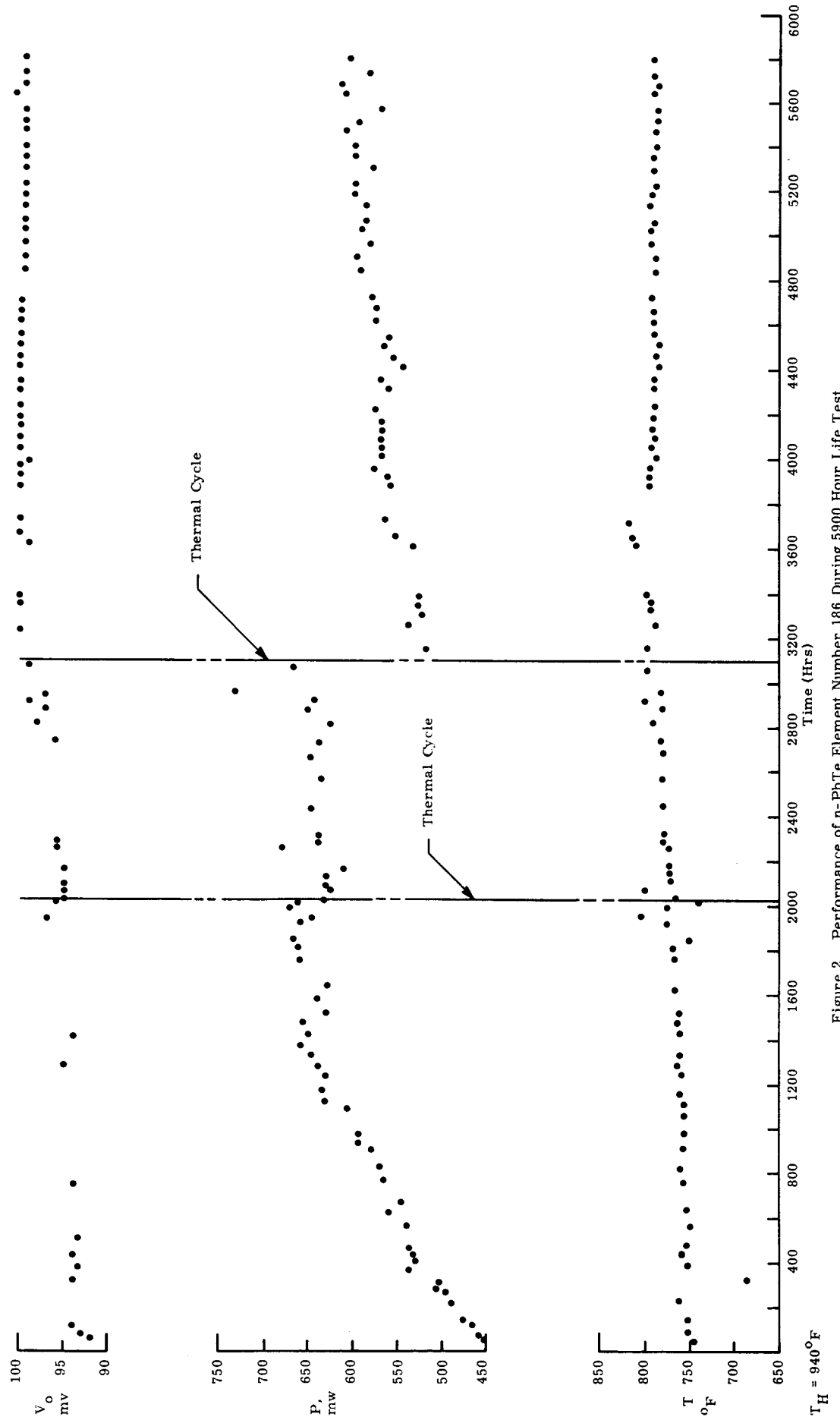
Figure 2. Performance of n-PbTe Element Number 186 During 5900 Hour Life Test
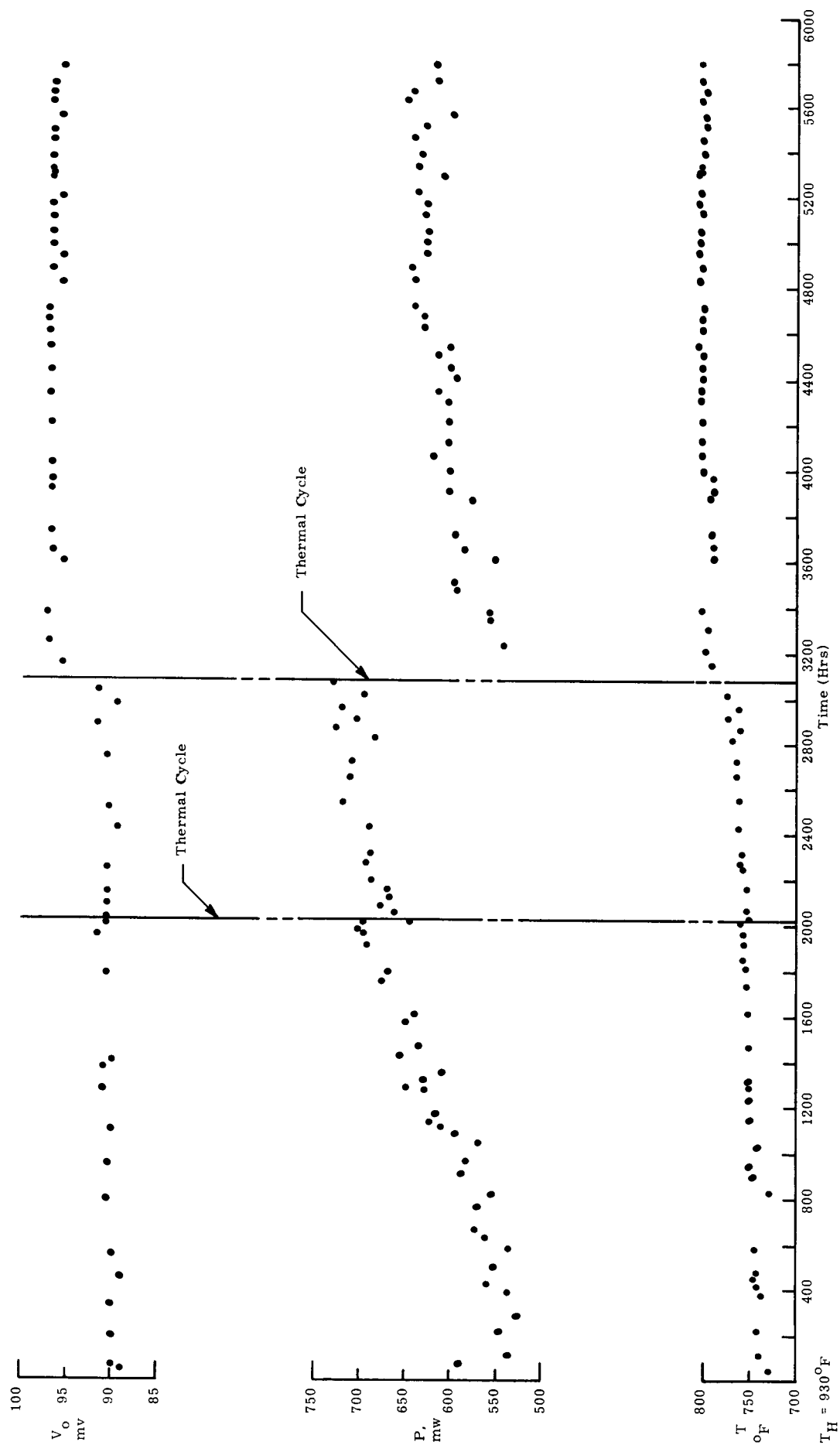
Figure 3.   Performance of n-PbTe Element Number 189 During 5900 Hour Life Test
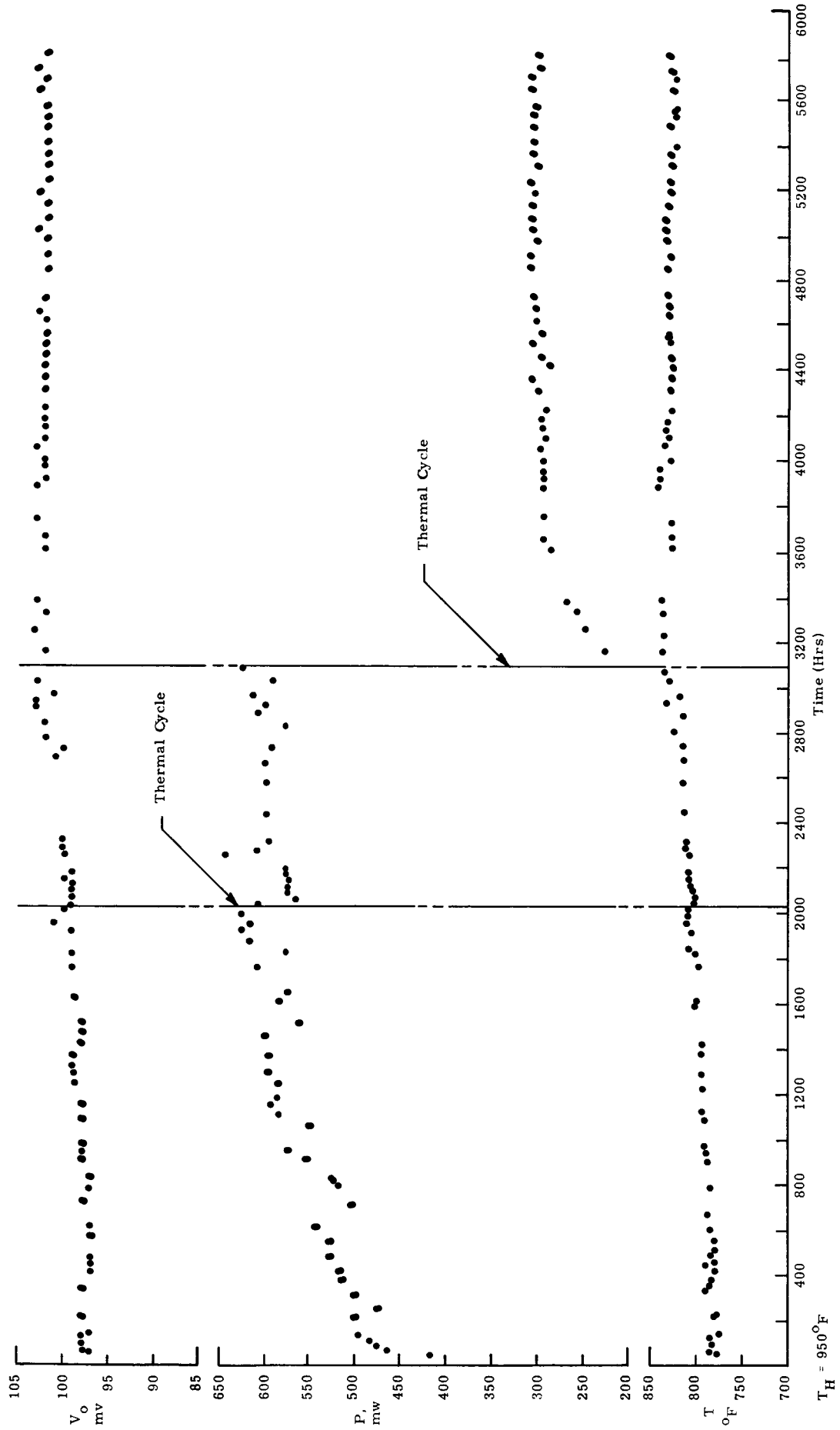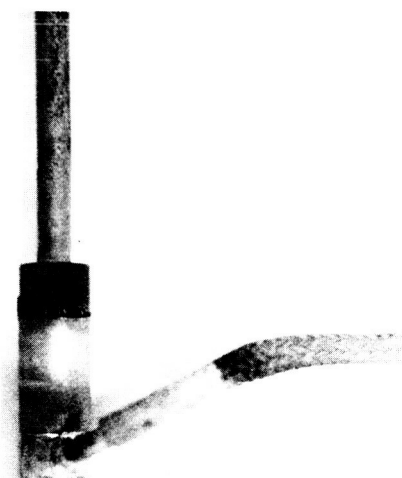
Figure 4. Performance of n-PbTe Element Number 197 During 5900 Hour Life Test

189A
n-PbTe

Figure 5

Appearance of Element Number 189 After 5900 Hour Life Test

TABLE II

Properties of n-PbTe Thermoelectric Elements after 5900 Hour Life Test

Seebeck Coefficient Data

Sample No.	Composition	Bond Resistance, μΩ				Room Temp. Resistivity, μΩ·in			As Pressed			As Bonded			After Life Test		
		Before Test		After Test		As Pressed	As Bonded	After Life Test	Temp, °C	S, μV/°C	% deviation from 3M Values	Temp, °C	S, μV/°C	% deviation from 3M Values	Temp, °C	S, μV/°C	% deviation from 3M Values
		Hot	Cold	Hot	Cold												
202	TEG-2N n-PbTe	Contact	Contact	570	Contact	190	---	155	105 / 165	157 / 186	-14.2 / -9.7	--- / ---	--- / ---	--- / ---	66 / 98	174 / 192	+4.2 / +6.7
197	TEG-2N n-PbTe	70	63	40	Separated	164	171	179	104 / 160	165 / 189	-9.3 / -7.4	79 / 138	155 / 180	-9.9 / -8.2	76 / 108	165 / 185	-3.5 / +0.5
3M-3	TEGS-2N n-PbTe	Contact	Contact	420	Contact	192	---	167	97 / 157	162 / 193	-9.5 / -4.9	--- / ---	--- / ---	--- / ---	63 / 96	164 / 177	-1.2 / -1.2
186	TEG-2N n-PbTe	48	0	80	0	182	170	169	102 / 162	164 / 188	-9.4 / -8.3	89 / 138	154 / 176	-12.5 / -13.3	62 / 98	141 / 165	-14.5 / -8.3
3M-2	TEGS-2N n-PbTe	40	Contact	50	Contact	193	174	181	96 / 152	164 / 184	-8.4 / -8.5	92 / 139	154 / 173	-13.0 / -11.7	60 / 88	126 / 154	-23.7 / -12.5
189	TEG-2N n-PbTe	40	5	50	50	169	171	185	95 / 149	176 / 195	-1.7 / -2.5	93 / 143	156 / 176	-12.4 / -11.1	62 / 95	152 / 165	-7.9 / -7.8

the braze. Figure 6a, a photomicrograph of element 3M-2 shows both these effects and Figure 6b, which shows the bond zone of element 197, displays only the oxide dispersion within the braze. The diffusion bonds formed during test in the initially unbonded thermoelements were also oxidized as can be seen in Figure 7. As was noted above, despite the observed oxidation, bond resistance was unaffected in the braze bonded samples.

Two samples from this group were sent to GSFC for study in the electron microprobe. As in previous samples extensive diffusion of tin into the lead telluride was observed. In this case tin was found to have penetrated at least 250 microns (0.010 inch) into the thermoelectric material. As was observed in other tests of n-PbTe, this diffusion had no effect on the performance of these elements.

A test of six bonded n-PbTe elements has been operating for 4000 hours and is continuing. Five of this group were fabricated at Hittman Associates while the sixth was purchased from 3M and bonded at our facility. Data for five of these elements have been routinely acquired and are reproduced as Figures 8 through 12. An apparent calibration error prevented acquisition of meaningful data from the sixth sample. As can be seen from the figure, the performance of these elements, particularly #392 and #404 has been affected by a series of thermal cycles.

C. Life Tests of p-PbTe

Two long term life tests of p-PbTe were conducted during this phase. One was a test of six p-PbTe elements which was terminated following a temperature excursion to 1500°F after 3576 hours of operation. The second is a test of six similar elements still in operation after having logged 5700 hours by October 1.

The 3576 hour test containing three hot pressed TEG-2P thermoelements and three similar elements each containing one percent by weight of fine molybdenum wires. The performance data for these element are shown in Figures 13 through 18. These curves indicate that the rate of power decline with time diminished to the point where in the last 1000 hours of operation the maximum drop in power was less than five percent.

The severe temperature excursion to which these elements were subjected made post-test property measurements of dubious value. Such measurements were made, however, and are reported in Table III. All elements but one were intact upon removal from the tester, the exception being element #315 from which the cold shoe had separated. In each element bond resistances were sharply higher than the pre-test values, with greater increase in those elements containing the molybdenum additive. Electrical resistivity declined in two samples and increased in the other four. There was a disparity in Seebeck coefficient measurements between those elements with no additive and those containing one percent molybdenum; the former showed a sharp decline in low temperature Seebeck coefficient while the latter displayed a comparable increase in this parameter. Since the two groups of elements behaved quite similarly during the course of the life test, it is likely that the observed behavior resulted from the temperature excursion that caused termination of the test. Controlled experiments would be needed to finally resolve this point however.

Fe   PbTe
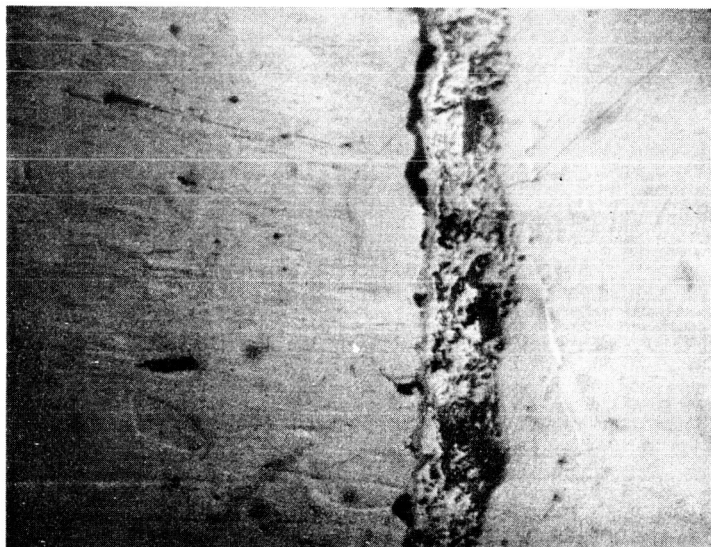
a) Element #3M-2   260X
    Mount #1420

Fe   PbTe
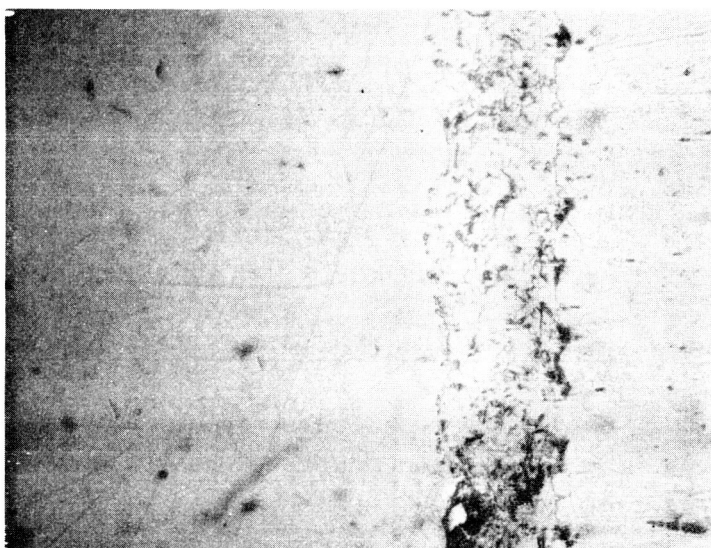
b) Element #197   260X
    Mount #1417

Figure 6

Appearance of Bond Zone in Brazed n-PbTe Elements After 5900 Hour Life Test

Fe   PbTe

Element #202   260X
Mount #1421

Figure 7

Appearance of Diffusion Bonded Interface Between Iron and n-PbTe
Formed During 5900 Hour Life Test
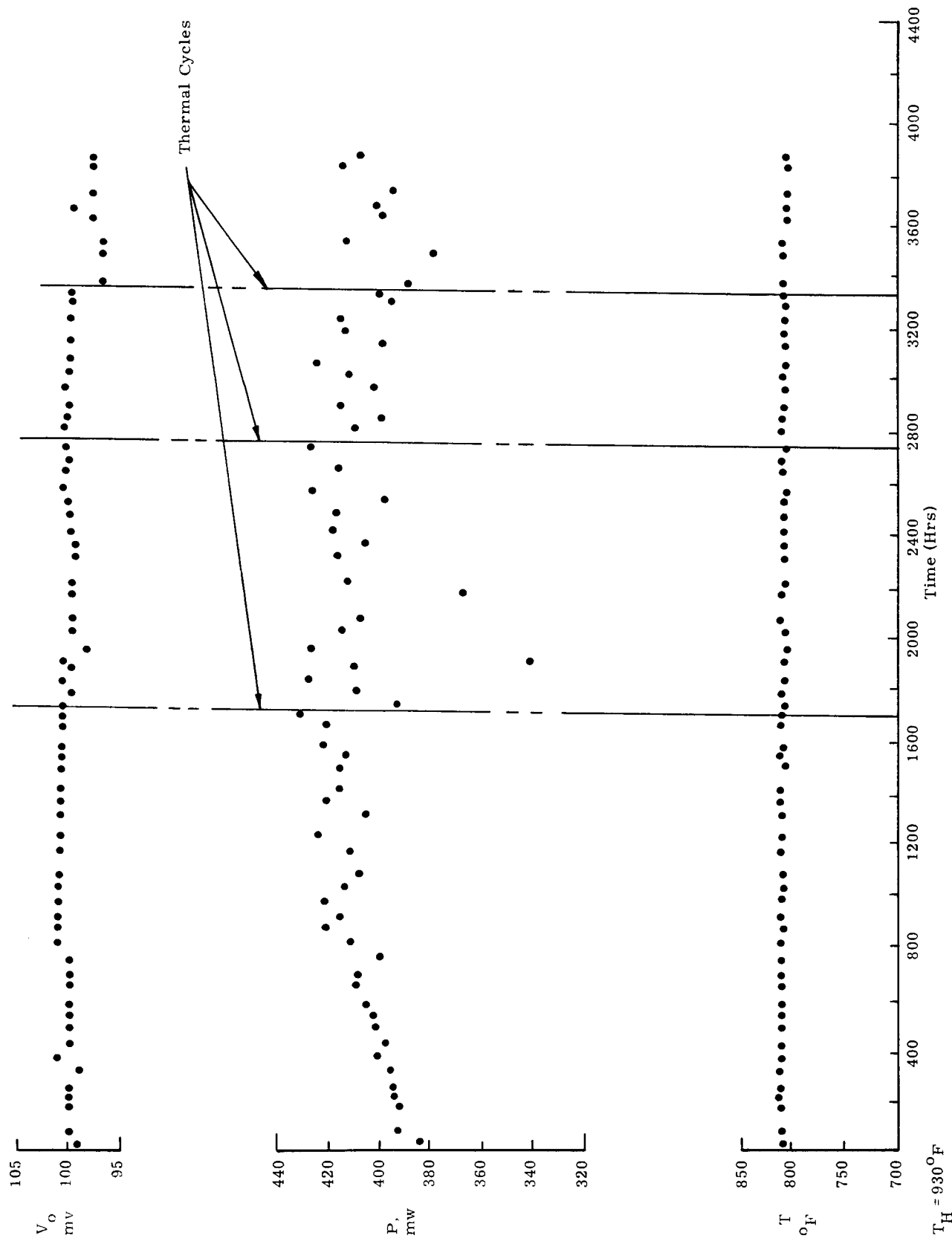
Figure 8.   Performance to Date of n-PbTe Element Number 3M#5
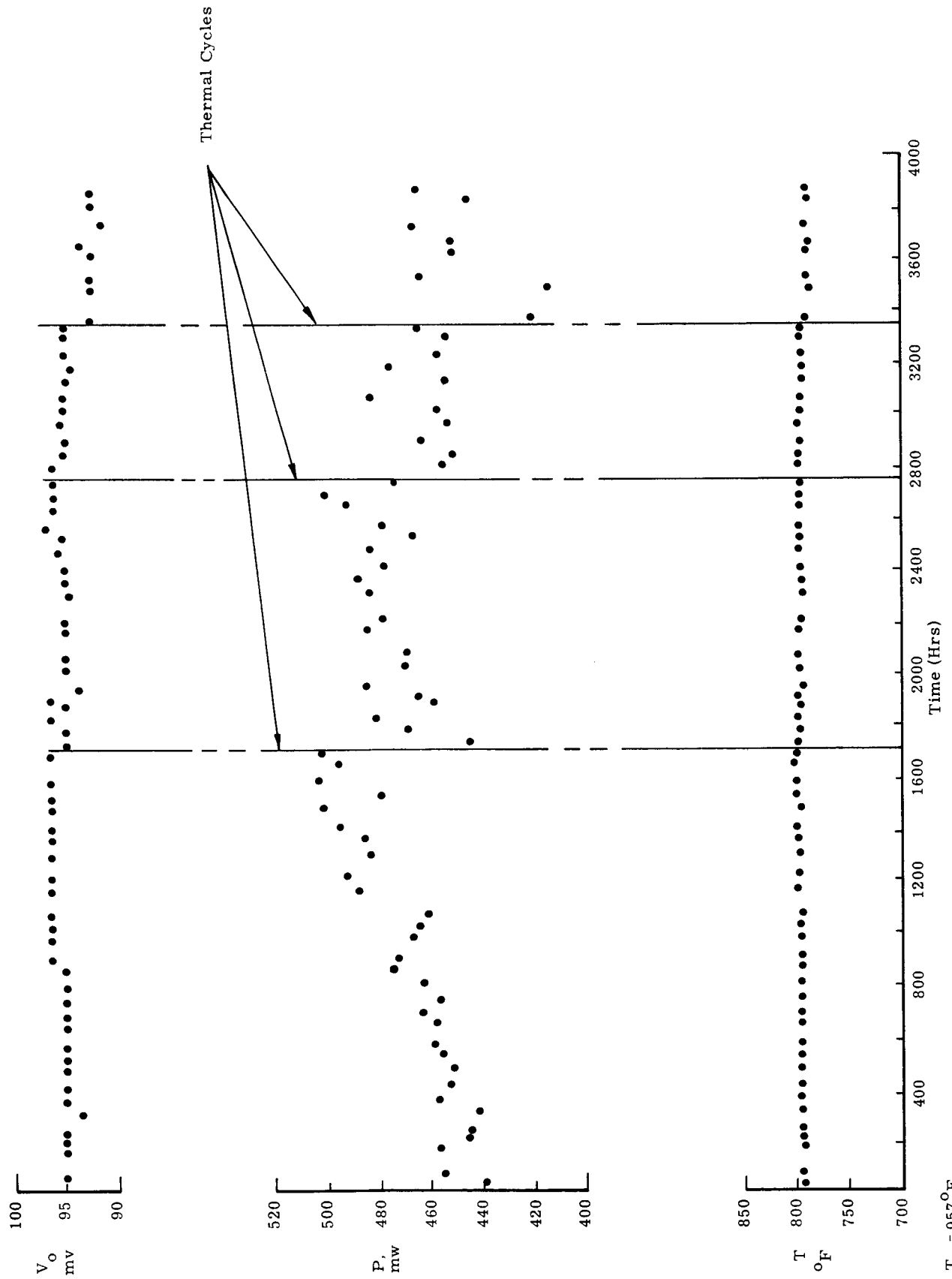
Figure 9. Performance to Date of n-PbTe Element Number 400

$T_H = 957^{\circ}F$
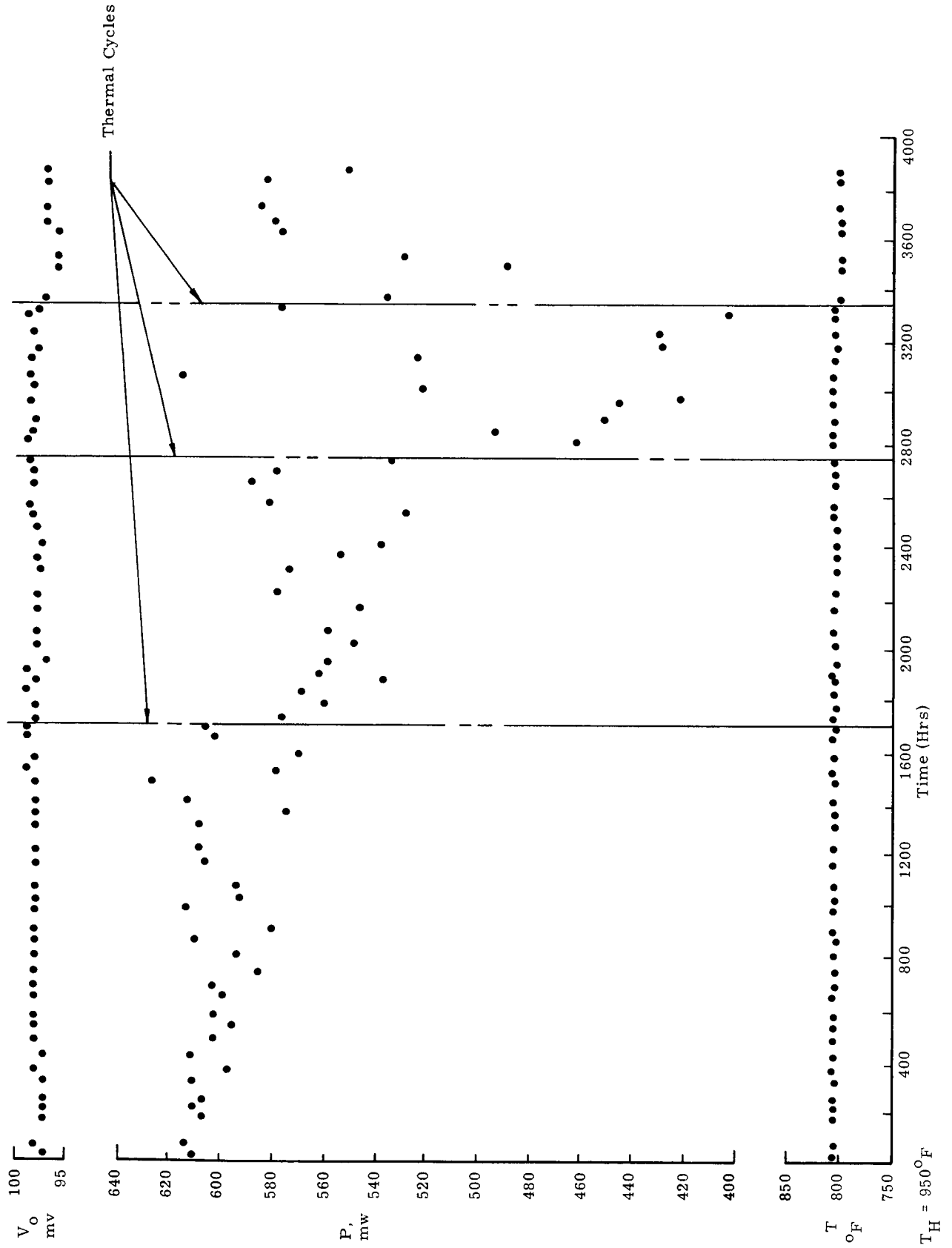
Figure 10.   Performance to Date of n-PbTe Element Number 392
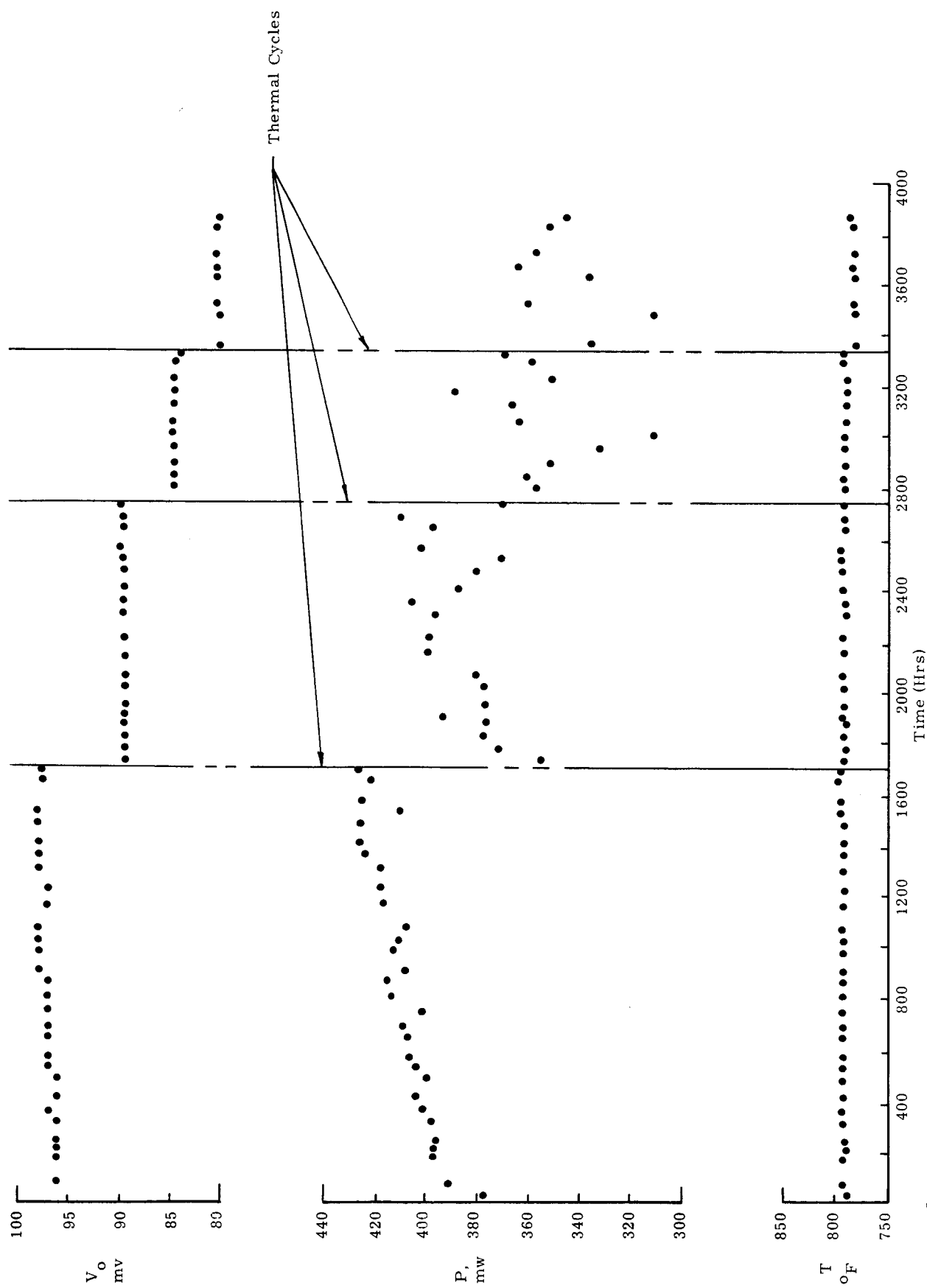
Figure 11. Performance to Date of n-PbTe Element Number 379
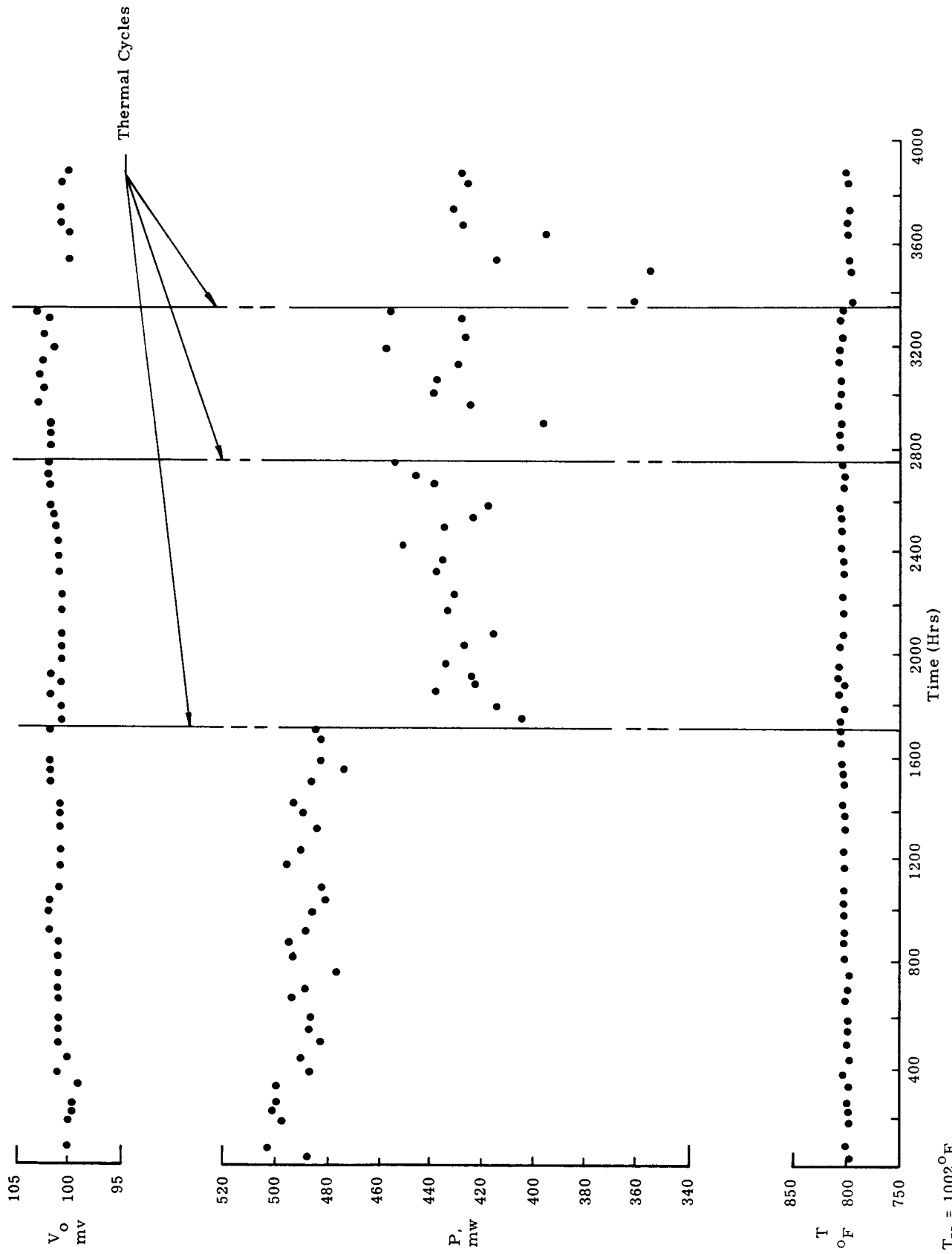
Figure 12. Performance to Date of n-PbTe Element Number 404
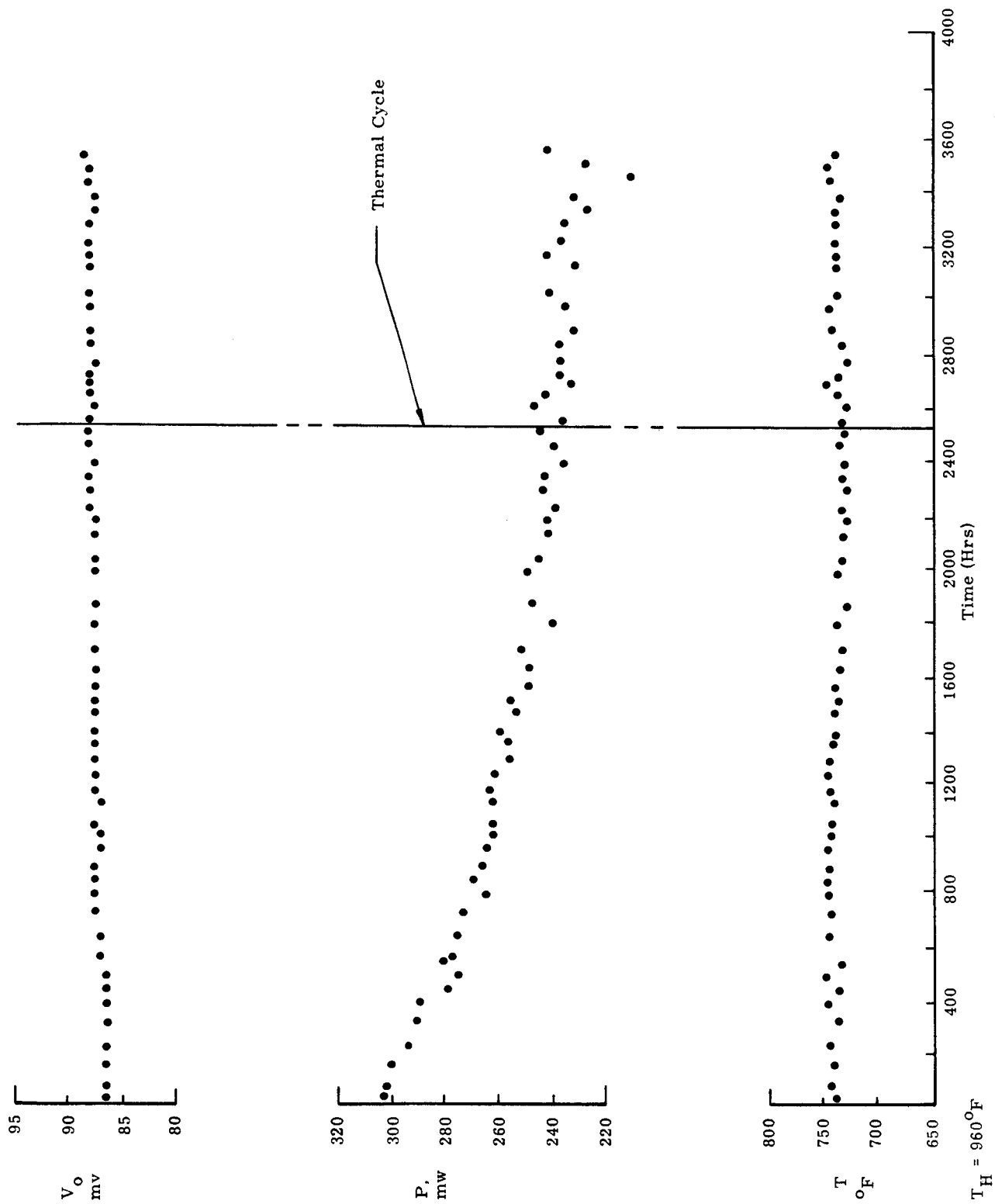
Figure 13. Performance of p-PbTe Element Number 362 During 3576 Hour Life Test (TEG-2P)
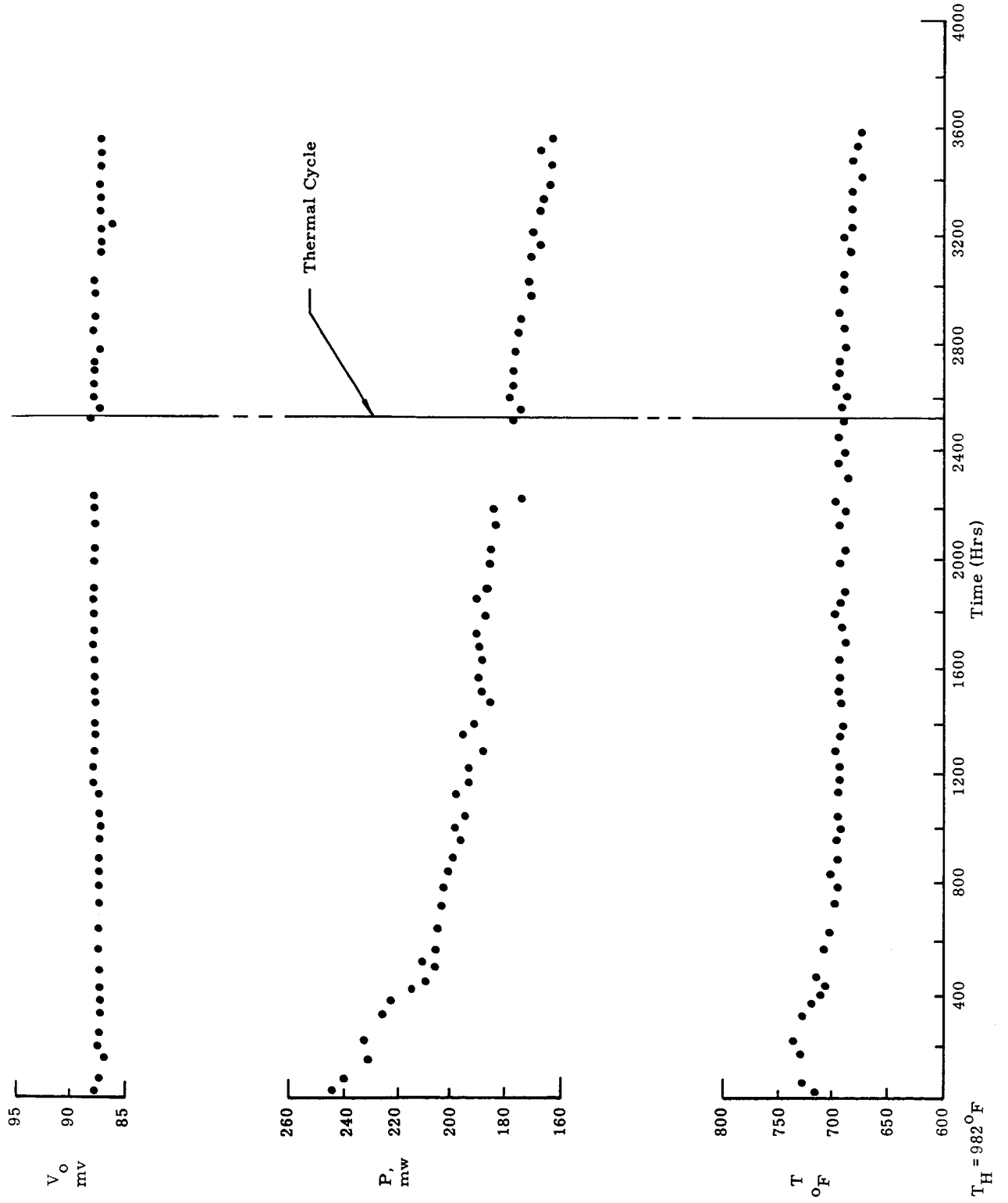
Figure 14. Performance of p-PbTe Element Number 357 During 3576 Hour Life Test (TEG-2P)
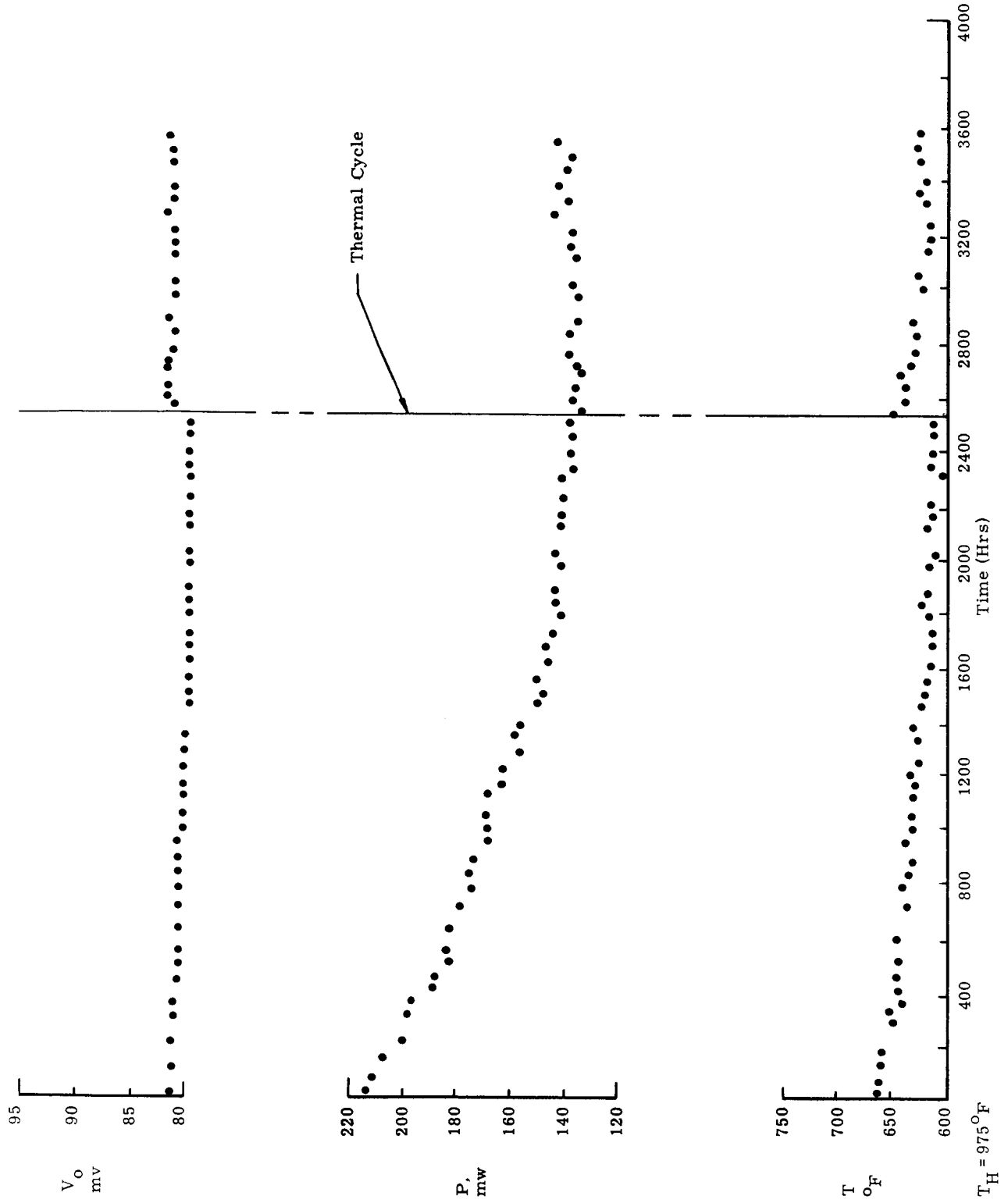
Figure 15. Performance of p-PbTe Element Number 352 During 3576 Hour Life Test (TEG-2P)
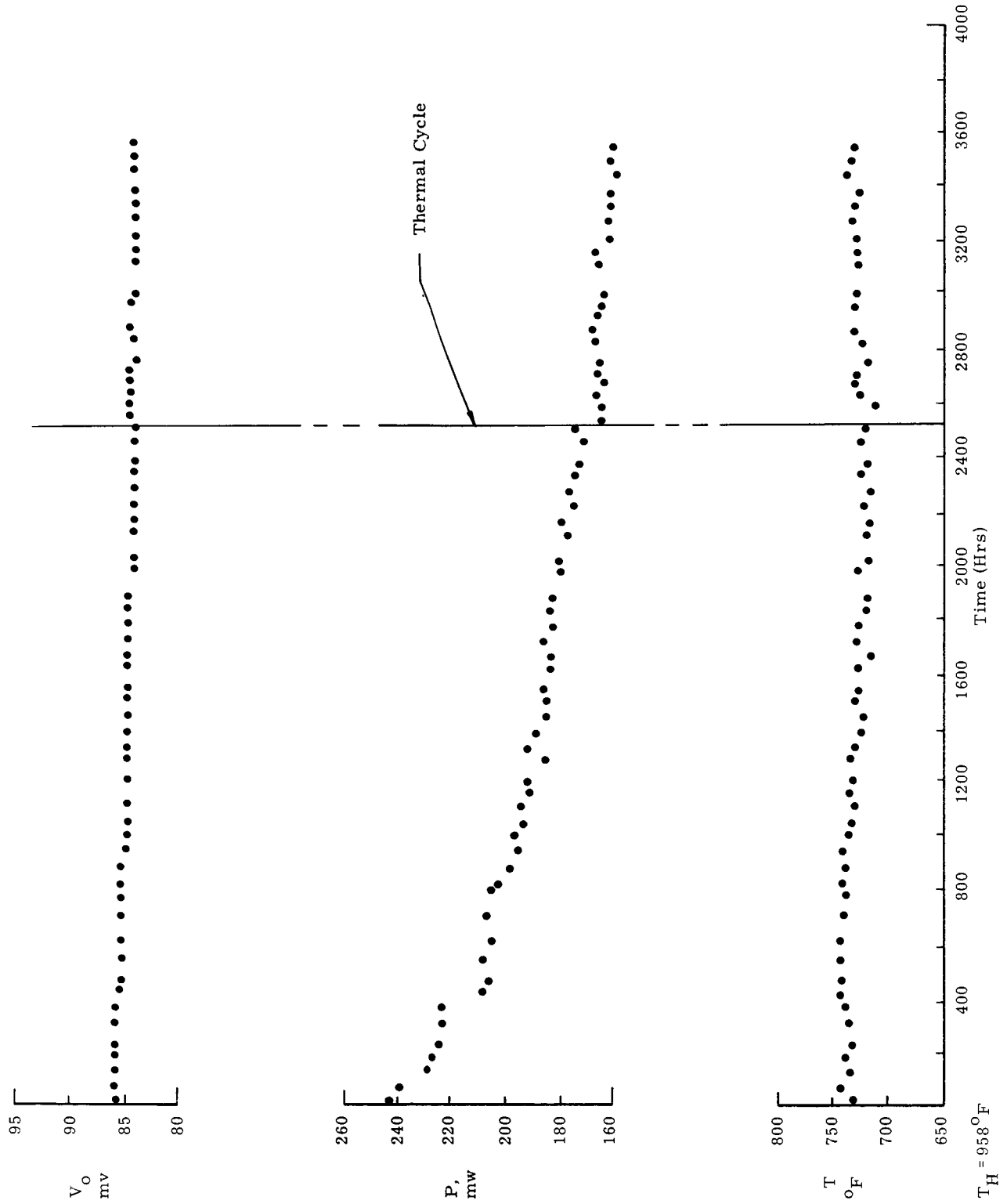
Figure 16. Performance of p-PbTe Element Number 328 During 3576 Hour Life Test (TEG-2P + 1% Molybdenum Fibers)
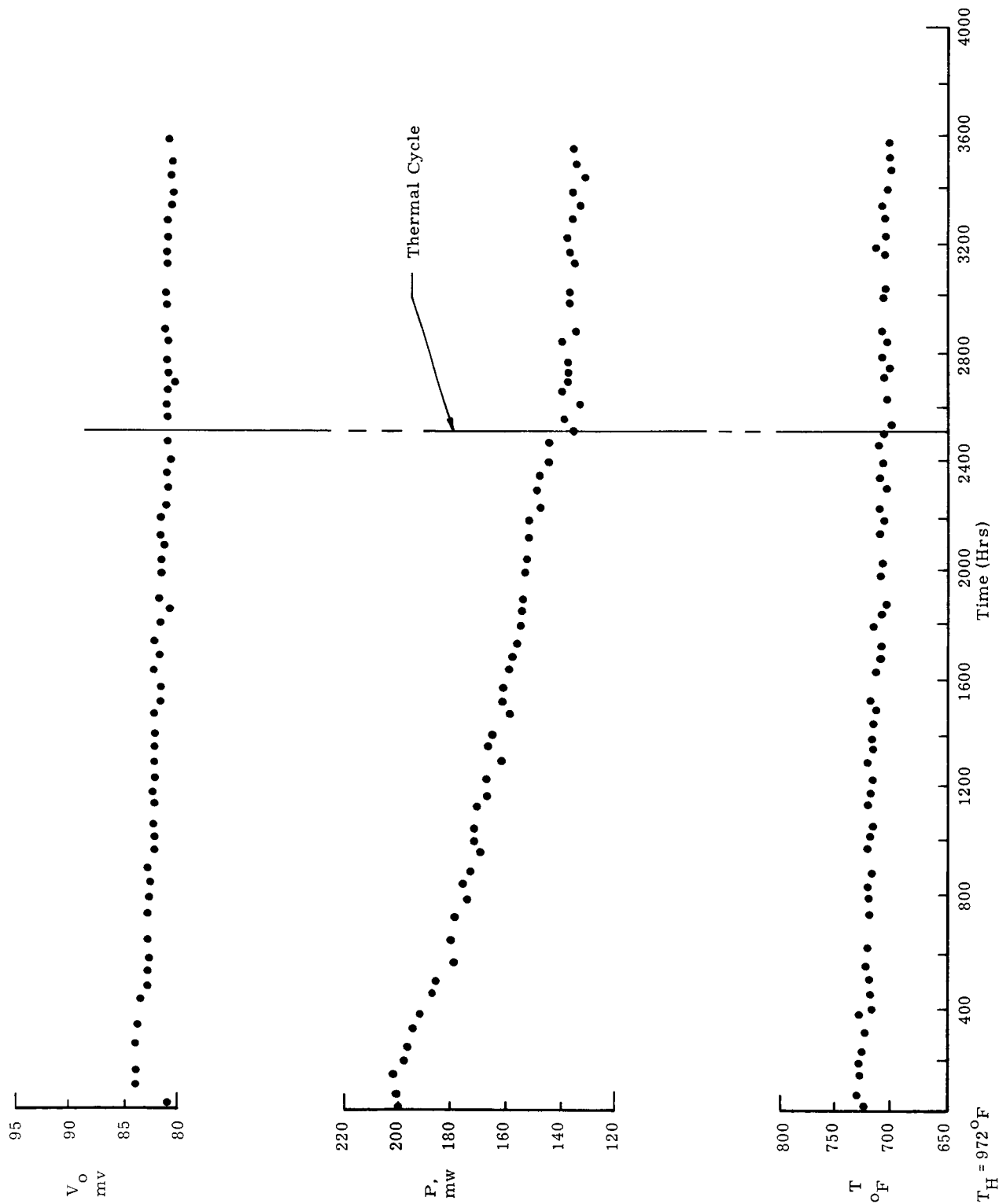
Figure 17. Performance of p-PbTe Element Number 308 During 3576 Hour Life Test (TEG-2P + 1% Molybdenum Fibers)
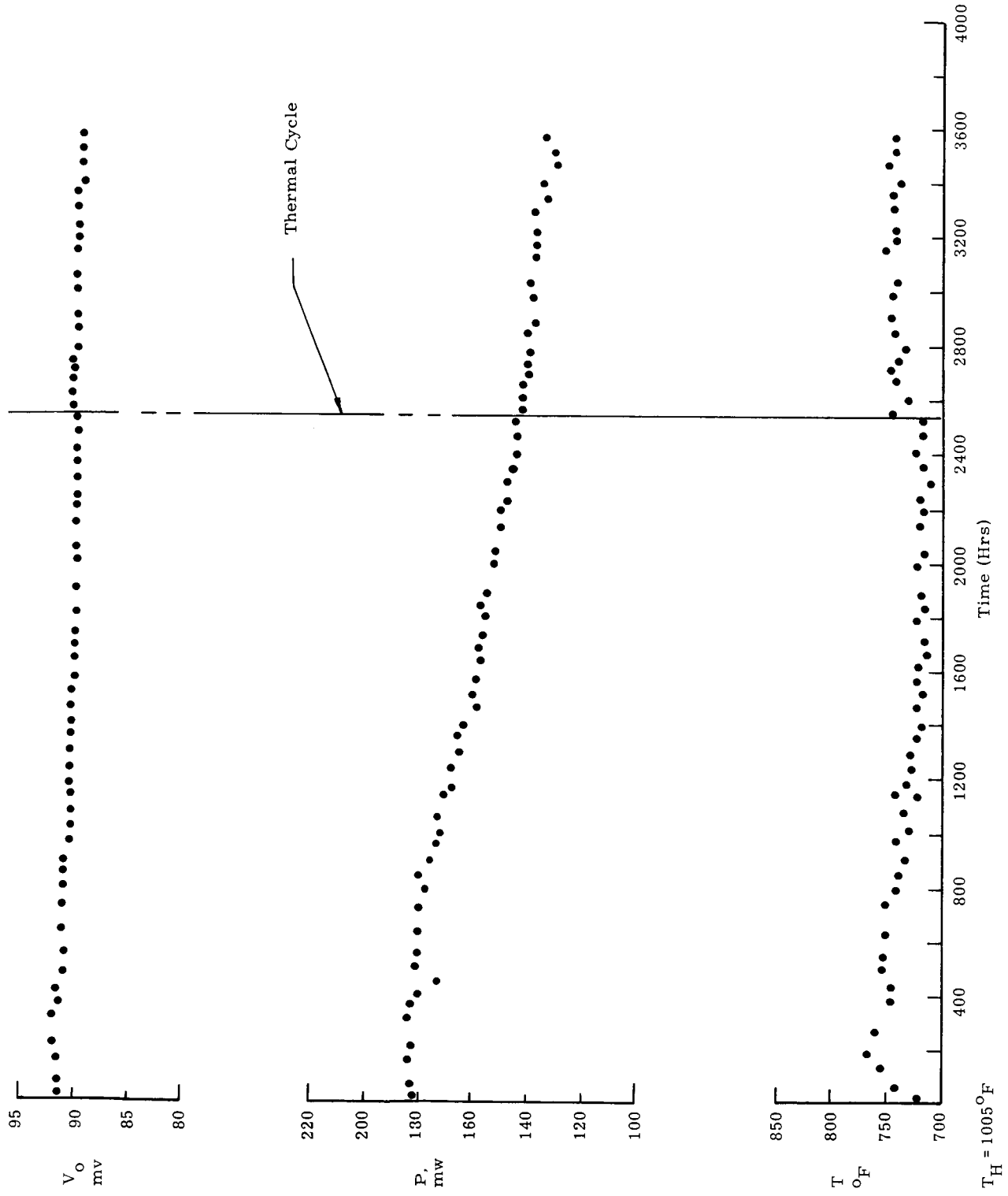
Figure 18. Performance of p-PbTe Element Number 315 During 3576 Hour Life Test (TEG-2P + 1% Molybdenum Fibers)

TABLE III

Properties of n-PbTe Thermoelectric Elements after 3576 Hour Life Test

| Sample No.	Composition	Bond Resistance, μΩ — Before Test Hot	Before Test Cold	After Test Hot	After Test Cold	Room Temp. Resistivity, μΩ·in — As Pressed	As Bonded	After Life Test	Seebeck Coefficient Data — As Pressed Temp, °C	As Pressed S, μV/°C	As Pressed % deviation from 3M Values	As Bonded Temp, °C	As Bonded S, μV/°C	As Bonded % deviation from 3M Values	After Life Test Temp, °C	After Life Test S, μV/°C	After Life Test % deviation from 3M Values
362	TEG-2P p-PbTe	0	10	75	350	160	178	173	101 / 167	91 / 138	-17.3 / -8.0	86 / 130	87 / 113	-13.0 / -12.4	82 / 129	64 / 80	-33.7 / -37.5
357	TEG-2P p-PbTe	60	65	75	275	200	167	200	98 / 149	100 / 138	-7.4 / 2.8	82 / 131	93 / 114	-4.1 / -12.3	80 / 134	66 / 86	-31.2 / -34.8
352	TEG-2P p-PbTe	130	80	250	725	158	161	178	104 / 164	100 / 138	-10.7 / -9.2	76 / 124	84 / 112	-9.7 / -10.4	96 / 151	73 / 98	-31.2 / -31.4
328	p-PbTe + 1 w/o Mo Wire	100	60	1140	350	159	195	164	80 / 143	91 / 137	-5.2 / -0.7	73 / 120	85 / 113	-6.6 / -7.4	68 / 106	99 / 128	+12.5 / +13.3
308	p-PbTe + 1 w/o Mo Wire	90	108	1380	450	152	162	180	101 / 153	98 / 135	-10.9 / -6.3	82 / 123	91 / 117	-6.2 / -5.6	72 / 109	103 / 128	+14.4 / +11.3
315	p-PbTe + 1 w/o Mo Wire	75	75	850	Separated	160	158	189	88 / 139	77 / 114	-23.8 / -15.6	83 / 122	89 / 119	-9.2 / -4.0	76 / 110	108 / 133	+16.1 / +15.4

The operating test of p-PbTe elements also consists of three p-PbTe elements containing one percent molybdenum wire and three elements without this additive. Performance to date of these elements is shown in Figures 19 through 24. The cause of the sudden increase in power of element #249 (Figure 21) following a thermal cycle induced by heater failure is not at present assignable. However, the smaller changes in output following this thermal cycle at 4300 hours are due principally to changes in hot junction temperature that resulted from the present operation with one heater as opposed to two heaters prior to the failure.

Electron microprobe studies at GSFC on p-PbTe samples tested for periods of 1, 500, 1745 and 3576 hours demonstrates a consistent pattern of diffusion of tin from the braze into the lead telluride. The depth of penetration of tin into the thermoelectric increased with time and the rate of penetration decreased with time. Approximate values of extent of diffusion are as follows:

Time at 950° - 1000°F hours	Maximum Tin Penetration microns
0	0
500	120
1745	175 - 200
3576	210 - 230

These results are typical of what would be expected in a diffusion reaction. If, as postulated previously, the degradation of p-PbTe elements is related to poisoning by diffusion of tin from the braze then a constantly decreasing rate of degradation would be expected. This is indeed what has been observed in the most recent long term tests as shown in Figures 13 through 24.

Figure 19. Performance to Date of p-PbTe Element Number 339 (TEG-2P)

Figure 20. Performance to Date of p-PbTe Element Number 348 (TEG-2P)

Figure 21. Performance to Date of p-PbTe Element Number 249 (TEG-2P)

Figure 22. Performance to Date of p-PbTe Element Number 327
(TEG-2P + 1% Molybdenum Fibers)

Figure 23. Performance to Date of p-PbTe Element Number 325
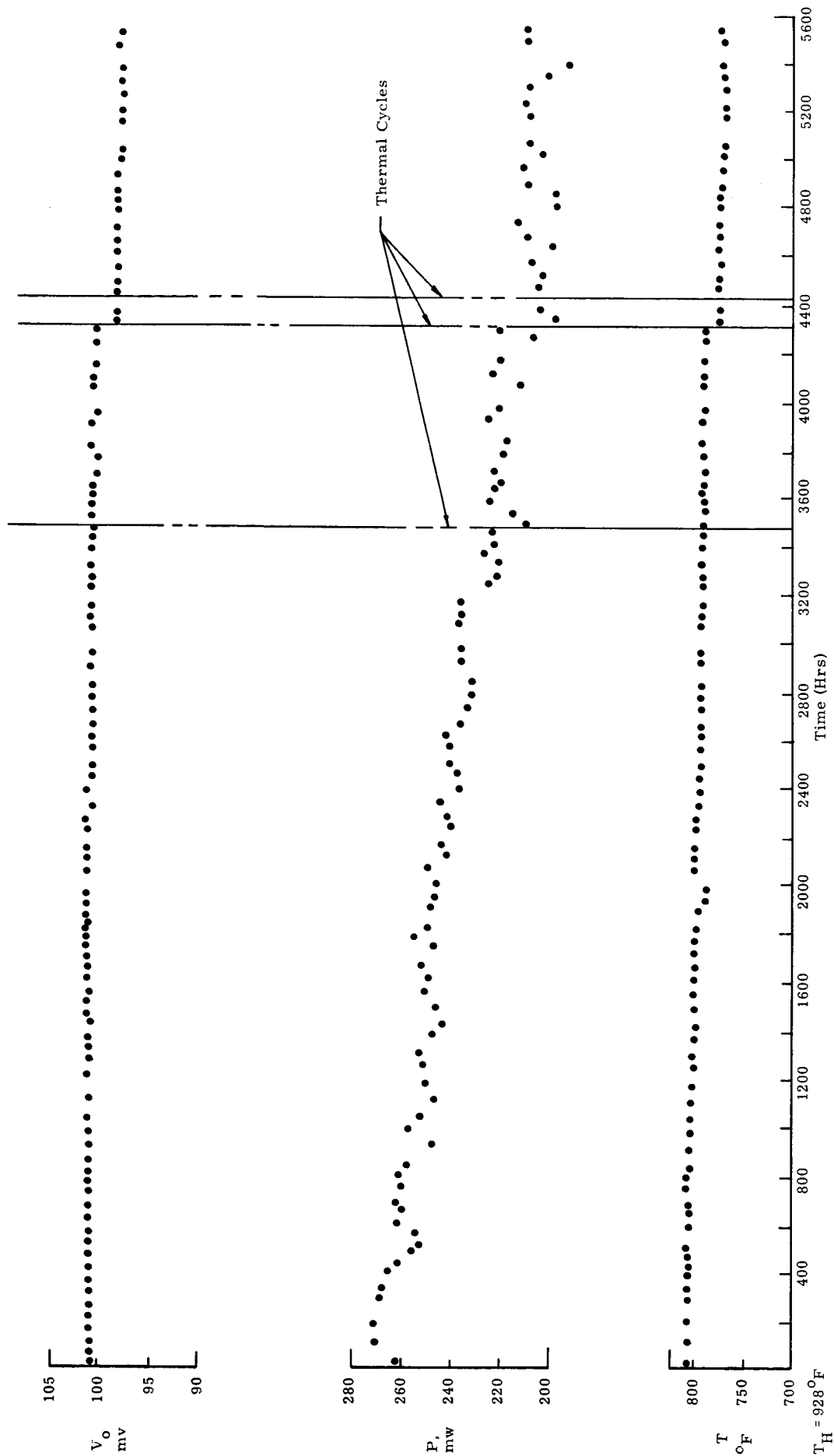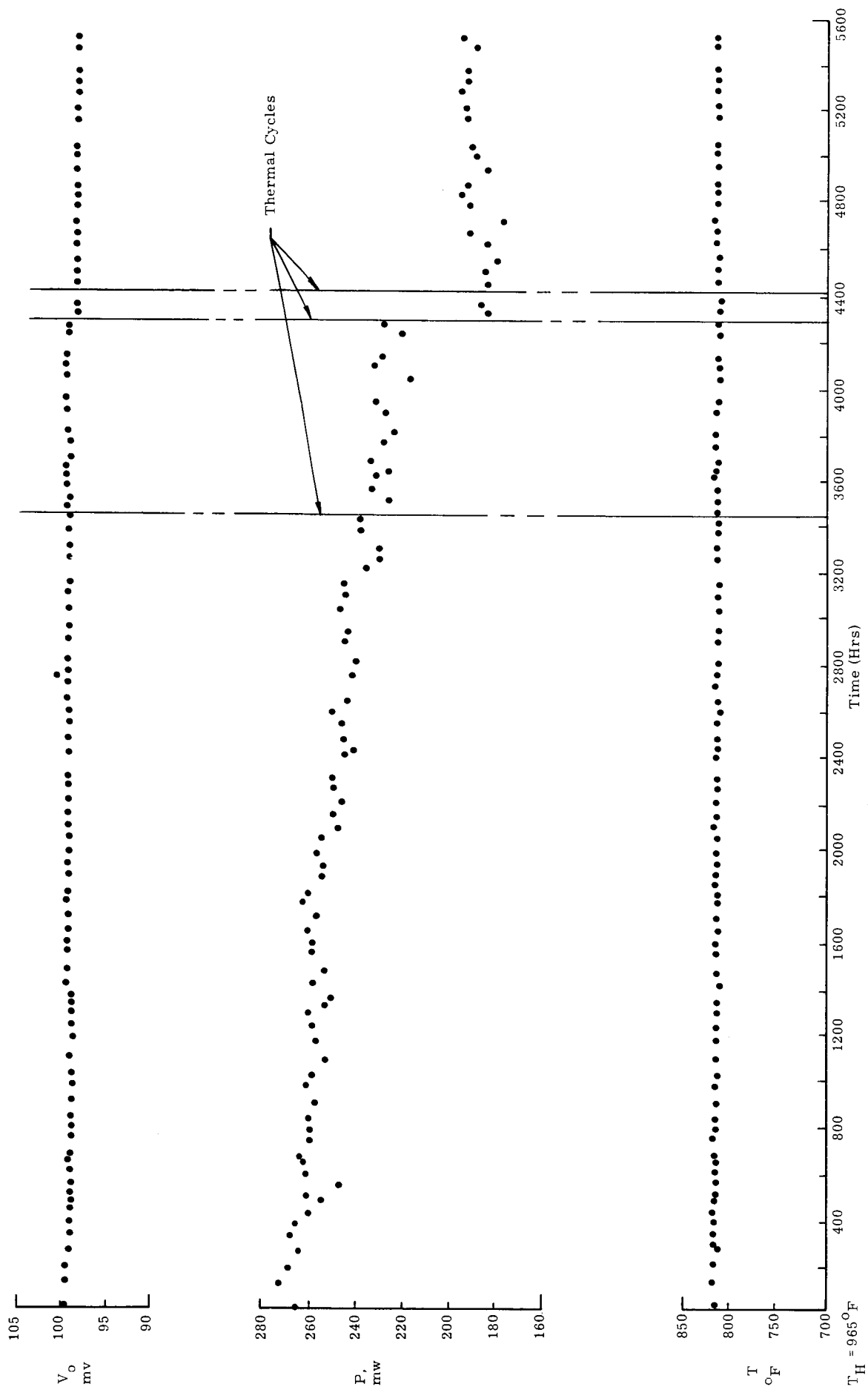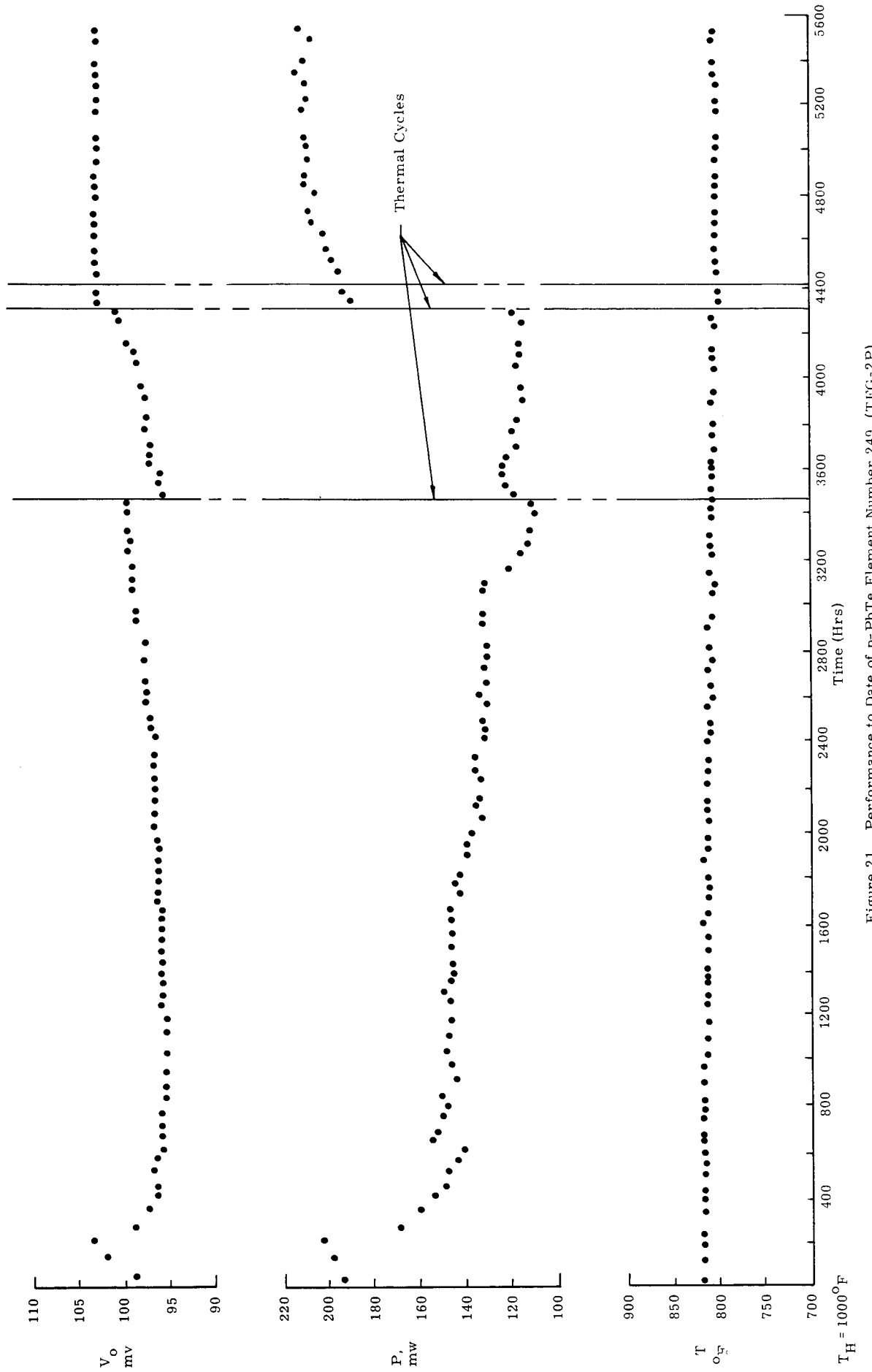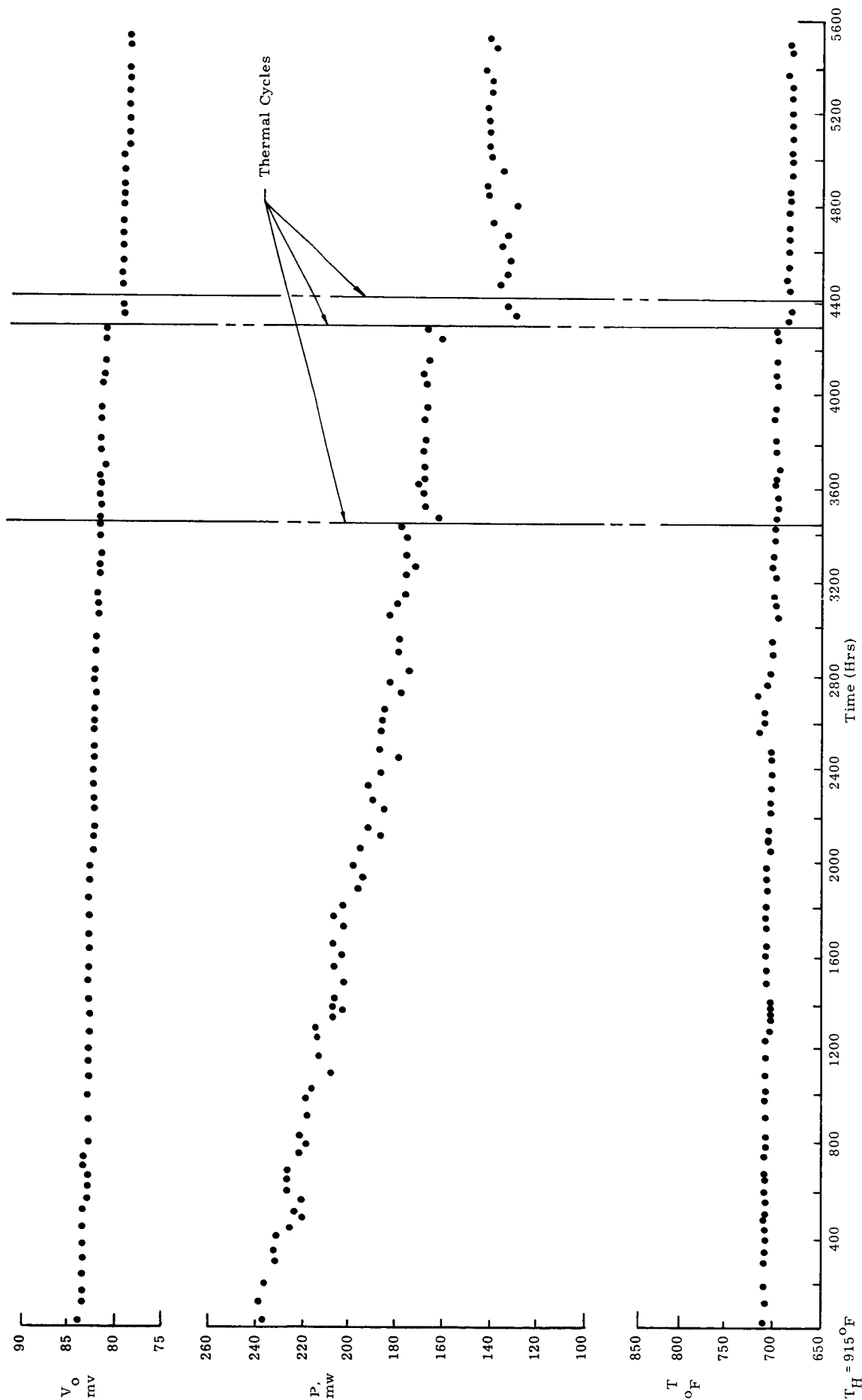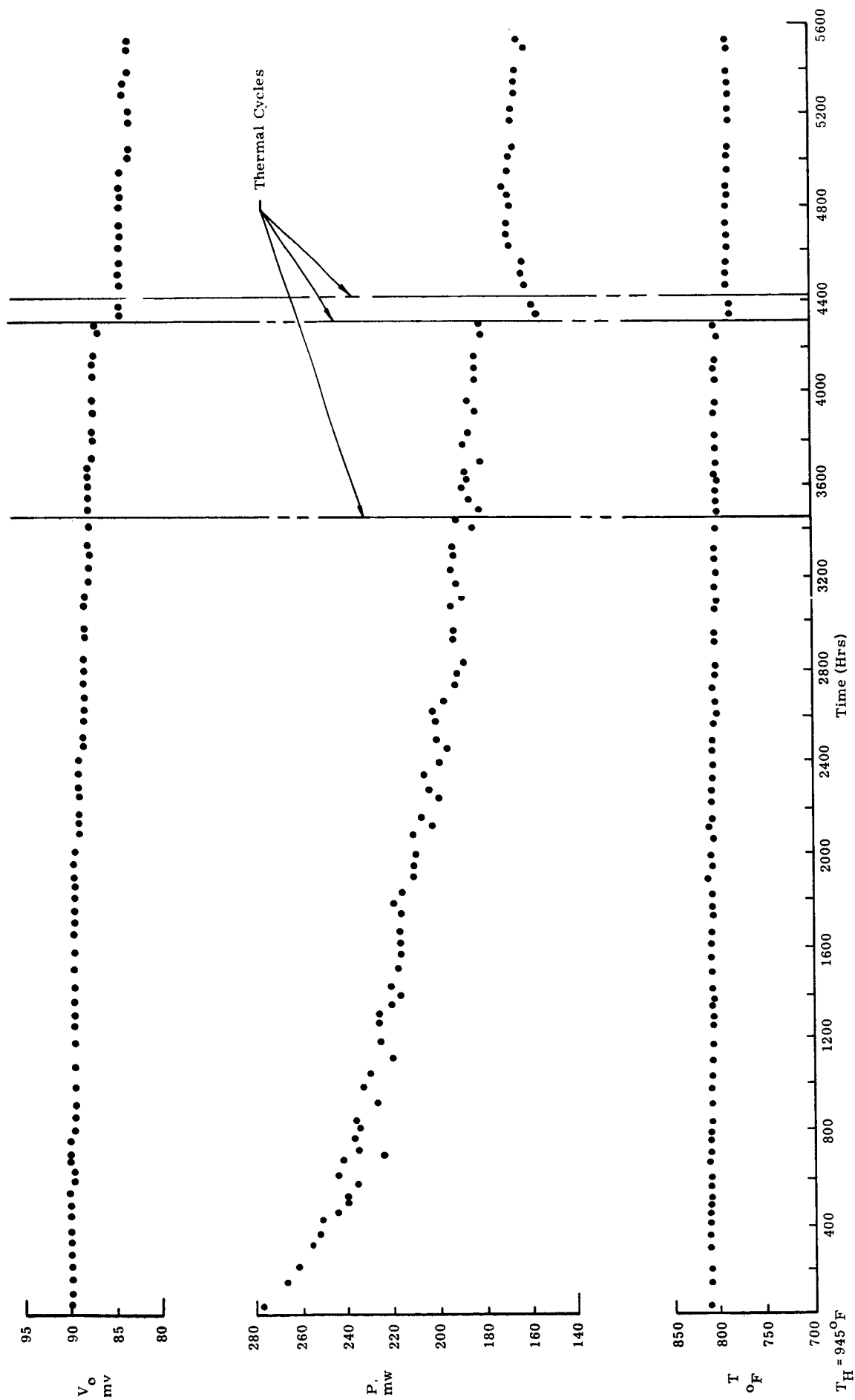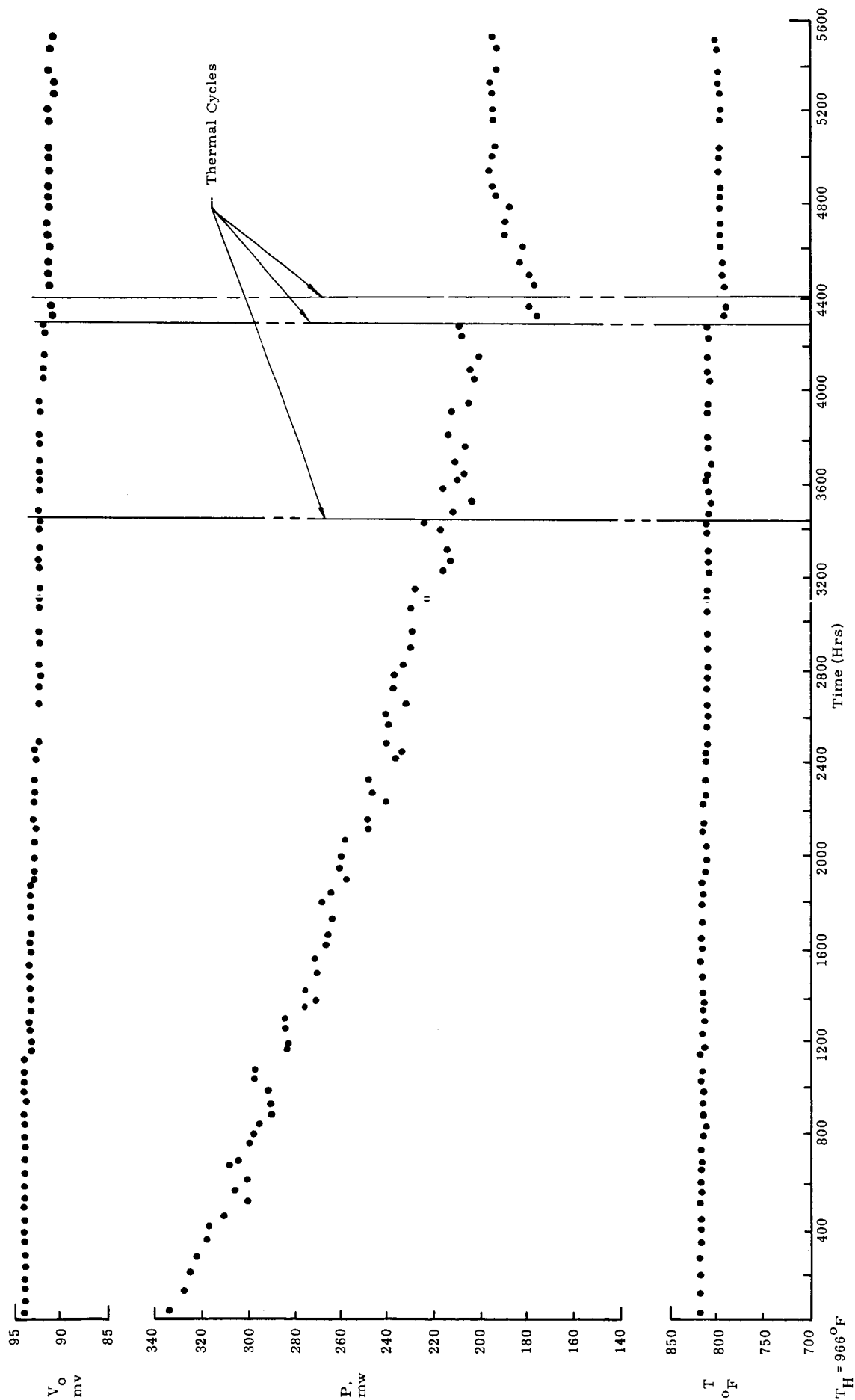(TEG-2P + 1% Molybdenum Fibers)

Figure 24. Performance to Date of p-PbTe Element Number 305
(TEG-2P + 1% Molybdenum Fibers)

IV. EFFECT OF ADDITIVES ON PROPERTIES p-PbTe

Early in this program it was demonstrated that p-PbTe is substantially weaker than the n-type material and that this inherent property frequently leads to cracking and breakage during bonding and subsequent handling. In order to treat this problem the possible strengthening effects on p-PbTe of several metal and oxide additives were studied during the previous phase. The results, reported in Reference 1, indicated that molybdenum and tungsten effectively strengthen p-PbTe and that Al_2O_3 in the form of sapphire fibers gave indications of similar performance.

Additional studies of these three additives were carried out as part of the current program. Three forms of molybdenum, fine wire and two powders were included in this investigation. Two diameters of wire and two powders comprised the tungsten additives. Several forms of alumina had been tested previously and of these only sapphire fibers appeared promising so our study was limited to this material. The additives tested are described in detail in Table IV. Two lots of p-PbTe powder, type TEG-2P purchased from 3M Company, were used in this study.

All test elements were produced in the form of hot pressed pellets 3/8 inch in diameter by approximately 3/4 inch high. The manufacturing procedure is similar to that used previously. The PbTe and additive powders were weighed out in a dry box. If the additive was tungsten or molybdenum wire these were first degreased and cleaned and cut into lengths of approximately 1/8 inch. Other additives were used as received. The ingredients were then mixed and placed in a clean graphite die. Separate dies were used for each additive listed in Table IV to prevent possible cross contamination of the hot pressed elements. New dies were first baked out at a temperature in excess of the hot pressing temperature to remove any volatiles that might be present. The ends of the die pins were lightly coated with Al_2O_3 to minimize sticking.

Hot pressing was carried out in an argon atmosphere at 1500^OF. Pressure of 2500 psi was held for 5 minutes and the elements were cooled to room temperature under load. The appearance of samples containing molybdenum or tungsten was generally sound with no cracks and few, if any, chipped corners. Elements containing Al_2O_3 and control samples without additives displayed more frequent cracking and chipping. The addition of Al_2O_3, in fact, made hot pressing more difficult and two of the four thermoelements made with the sapphire fibers broke during removal from the die or shortly thereafter.

A. Effect of Additives on Thermoelectric Properties

Room temperature resistivity and low temperature Seebeck coefficient were measured on all elements processed during this task. The results are summarized by type of additive in Table V. Because of wide differences in resistivity of the two lots of TEG-2P lead telluride powder used in these samples data are reported separately for each lot of powder. The first row in this table lists the properties of elements containing no additives. Typical of our previous experience and that of other investigators, measured resistivity and Seebeck coefficient values were below those published by 3M for this material and below the values supplied as quality control release data.

TABLE IV

Additives to p-PbTe Studied During This Phase

Additive	Form	Source
Molybdenum	-325 mesh powder, 99.9%	Consolidated Astronautics
Molybdenum	powder, mesh size not stated but appeared finer than the -325 mesh powder described above, 99.95%	United Mineral and Chemical
Molybdenum	0.001" diameter wire	Sylvania Electric Products
Tungsten	-325 mesh powder, 99.9%	Consolidated Astronautics
Tungsten	powder, mesh size not stated but appeared finer than the -325 mesh powder described above, 99.999%	United Mineral and Chemical
Tungsten	0.001" diameter wire	Sylvania Electric Products
Tungsten	0.0005" diameter wire	Sylvania Electric Products
Alumina	Sapphire fibers	Thermokinetic Fibers

TABLE V

Effect of Additives on Thermoelectric Properties of p-PbTe

Additive	Samples made from Lot 1047 TEG-2P Powder			Samples made from Lot 1089 TEG-2P Powder		
	No. of Samples	Av. Resistivity μΩ in	Av. Seebeck % Dev. from Pub. 3M Value	No. of Samples	Av. Resistivity μΩ in	Av. Seebeck % Dev. from Pub. 3M Value
No additives	15	171	- 8.3	13	141	- 7.4[1]
1% Mo Powder 99.9%	2	190	-19.5	6	129	-17.5
4% Mo Powder 99.9%	2	189	- 3.5	0	---	---
1% Mo Powder 99.95%	0	---	---	5	144	-14.3
2% Mo Powder 99.95%	1	231	- 9.0	5	145	-18.0
1% Mo Wire	5	179	-17.0	6	157	- 9.0
2% Mo Wire	2	198	- 7.5	0	---	---
4% Mo Wire	3	181	-24.3	0	---	---
1% W Powder 99.9%	2	173	- 9.0	6	142	- 9.1
4% W Powder 99.9%	2	168	+ 5.0	0	---	---
1% W Powder 99.999%	3	158	- 9.5[2]	5	125	- 8.7
2% W Powder 99.999%	3	184	- 6.3	5	132	-14.3
1% W Wire[3]	3	175	-12.7	6	130	-10.8
2% W Wire[3]	2	196	-11.0	0	---	---
4% W Wire[3]	5	218	-19.0	0	---	---
1/2% Al$_2$O$_3$ Fibers	1	315	- 5.0	0	---	---
1% Al$_2$O$_3$ Fibers	1	238	- 1.0	0	---	---

(1) Two samples with unusually high Seebeck coefficient omitted
(2) One sample   "   "   "   "   "   "
(3) Results are combined for 0.0005" and 0.001" diameter W wire

From Table V it can be seen that molybdenum tends to increase the resistivity of p-PbTe. This effect was fairly small and was almost nonexistent in samples made with powder from Lot #1089. There was an indication of small negative effects on the Seebeck coefficient. Tungsten, with the exception of samples containing 2 and 4 percent wire additives, had no effect on the resistivity of p-PbTe. Neither of the tungsten powder additives affected the Seebeck coefficient but wire additions had a slight negative effect. Since the total surface area of the wire additions is smaller than that of the powder additions, any changes in thermoelectric properties would normally be expected to be greater in samples in which the additive was in the powder form. Since this has not been observed, it may be concluded that the effects on thermoelectric properties caused by wire additions stem from impurities in the wire or surface contaminants not completely removed during cleaning.

Only four samples containing sapphire fibers were fabricated and of these, two broke before any measurements could be made. The electrical resistivity of the other two was unacceptably high, hence Al_2O_3 is no longer considered to be a promising additive and no further samples were produced.

Several of the samples discussed above were life tested for 1000 hours at hot junction temperatures of $950^o - 1000^oF$. The first test of six elements included p-PbTe containing four percent molybdenum powder, four percent molybdenum wire, one percent tungsten powder, one percent tungsten wire, one percent Al_2O_3 fibers and a control element without additives. During the 1000 hours of operation both samples containing tungsten, the elements containing molybdenum wire and the unmodified control remained within ten percent of their initial power. The sample containing molybdenum powder suffered a decline in output of thirty percent within the first 200 hours of operation and then remained relatively stable during the remaining 800 hours. Power drop was about ten percent of the 200 hour value during this period. The element containing Al_2O_3 declined erratically for the first 600 hours to about 80 percent of its initial value and held fairly steady from that point to the conclusion of the test. The most significant observation made during post-test evaluation was that bond resistance increased in all elements, most markedly in that element containing molybdenum powder. Seebeck coefficient changes were small in all samples and only in the element containing Al_2O_3 did resistivity show a marked increase.

A second 1000 hour test was carried out with similar results. This group consisted of p-PbTe elements containing one percent molybdenum power, two percent tungsten powder, four percent tungsten wire and a control with no additive. All but the element containing molybdenum powder performed stably showing only modest declines in power output during the test period except for discontinuous drops caused by drastic thermal cycles (resulting from a series of power failures). The single exception declined by about fifteen percent during the initial 400 hours but showed no further degradation during the test. The severe thermal cycling mentioned above is the probably cause of shoe separation that occurred in all samples during removal from the tester. The hot shoe was found to be separated from all four of the test elements while the cold shoes were intact. Resistances of the single intact bond was in every case higher than the pre-test value, but no more so then in other experiments in which bond failure was not observed.

A third group of elements is presently under test. However, performance data are not yet available.

B. Effect of Additives on the Strength of p-PbTe

Several additional torsion tests were performed on p-PbTe thermoelectric elements containing molybdenum and tungsten additives. As in previous tests the elements were bonded to iron shoes each of which had a hex nut for gripping machined into one end. A typical torsion test sample is shown in Figure 25.

Table VI reports the results of torsion tests performed at room temperature and Table VII contains results of a series of tests carried out at 1000°F. At both temperatures the elements containing additives were stronger than p-PbTe without additives. Further, molybdenum is consistently more effective than tungsten in strengthening p-PbTe. These results are consistent with those reported earlier (Reference 1). However, the absolute value of the room temperature strengths measured recently appeared to be lower than those reported earlier. The lots of lead telluride powder used in these tests were checked and it was found that the samples reported in Reference 1 were made from powder identified by 3M Company as coming from Lots #1002 and #1047. Those elements whose properties are reported in Table VI were made from powder supplied as Lot #1089 except for the 4 percent molybdenum sample which used power from Lot #1047. This sample was substantially stronger than the others in this test group and while it was at first felt that the high strength was due to the large quantity of molybdenum, it may well be that the inherently greater strength of material from Lot #1047 compared to Lot #1089 contributed at least part of the observed difference.

During earlier work, samples of bonded p-PbTe were tested at 600° and 1000°F and it was observed that the strength was independent of test temperature (Reference 2). Comparison of the results reported in Tables VI and VII indicate, at first glance, that the samples tested at 1000°F during this program are considerably stronger than those tested at room temperature. However, the elevated temperature test samples were all fabricated from Lot #1047 powder. When the 1000°F results are compared with those reported at room temperature in Reference 1, the results are quite comparable except for the single element containing no additive which appears to be somewhat stronger than expected. Further tests will be required to resolve this anomalous lot to lot variation in properties.

The efficiency of molybdenum and tungsten in strengthening p-PbTe has been satisfactorily demonstrated despite the observed variation in data.
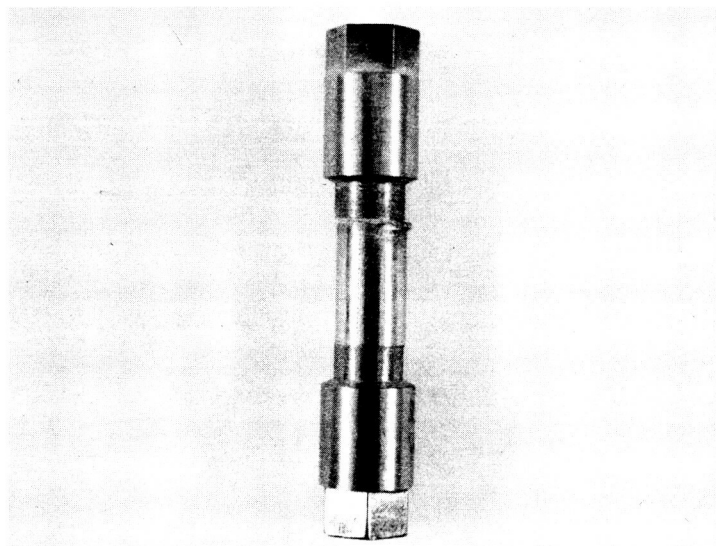
Figure 25

Torsion Test Specimen of PbTe Bonded to Iron Shoes

TABLE VI

Torsion Strength of p-PbTe Containing Additives
(Room Temperature)

Additive	Torsion Strength, psi	Remarks
p-PbTe no additive	400	Separated at braze interface
p-PbTe no additive	250	Broke within element
1% Mo Powder	700	Helical crack in element near braze
4% Mo Powder	1900	Helical fracture in element
1% Mo Wire	700	Helical fracture in element
1% Mo Wire	1000	Separated at braze interface
1% W Powder	550	Helical crack in element near braze
1% W Powder	600	Separated at braze interface
1% W Wire	500	Helical separation within element
1% W Wire	450	Helical separation within element

TABLE VII

Torsion Strength of p-PbTe Containing Additives
(1000°F)

Additive	Torsion Strength, psi	Remarks
p-PbTe no additive	850	Broke within element
4% Mo Wire	1800	Helical fracture
2% W Wire	950	Helical fracture
4% W Wire	1150	Helical fracture
4% W Wire	1100	Broke within element

V. BONDING OF LEAD TELLURIDE TO STAINLESS STEEL SHOES

The stress due to differences in the rate of contraction during cooldown is believed to be a major cause of cracking in bonded lead telluride thermoelectric elements. Iron, for example, expands or contracts at little more than one half the rate of lead telluride. Since austenitic stainless steels, i.e. 300 series stainless, have thermal expansion coefficients closely matching that of lead telluride, a preliminary study of bonding to stainless steel shoes appeared to be a logical step and was undertaken during the course of the program.

A number of experimental runs were performed. In each, three p-PbTe elements, hot pressed from the same lot of powder, were prepared for bonding by the procedures described previously in Reference 1. One was mated to iron hot and cold shoes and the other two to identical shoes machined from type 304 stainless steel. Three variations of the bonding process for p-PbTe described in Reference 1 were utilized. The first was an exact duplication of the standard process including cooling from the bonding temperature at 50°F per hour. In the second the rate of cooling was not controlled. Instead the inert atmosphere chamber in which bonding was carried out was removed from the furnace immediately after the five minute hold time at 1500°F was completed. Under these conditions the temperature declined initially at about 30°F per minute and cooled to below 400°F within one hour. The third procedure employed furnace cooling which resulted in an intermediate rate of temperature drop.

Visual observation of the specimens prepared by the two cycles with slow cooling showed that the iron shoes were bright and clean, typical of those previously bonded in this system. The stainless steel shoes were somewhat tarnished, having a dark oxide, presumably Cr_2O_3 on the surface. Measurements of thermoelectric properties before and after bonding showed no changes. Bond resistances were similar in elements bonded to iron and stainless steel, being less than 100 micro-ohms in almost all cases.

The rapid cooldown was attempted on two runs and was an unsatisfactory procedure. The appearance of the stainless steel shoes was better since they had been exposed to high temperature for a considerably shorter period of time. However, at least one bond on each element had very high resistance (several hundred micro-ohms) indicating that the thermal shock had caused cracking.

Torsion strength was measured on four p-PbTe elements bonded to stainless steel shoes by the standard process of Reference 1. The results, which are given in Table VIII, indicated measured strengths in three of the four samples well in excess of those typically found in p-PbTe bonded to iron shoes. The helical fracture pattern in these elements indicated the absence of cracks caused by bonding. This evidence leads to the conclusion that internal stress within the thermoelectric element is indeed reduced when a close match of thermal expansion between the thermoelectric material and shoe is achieved.

One element bonded to stainless steel shoes was life tested for 1000 hours, along with the second group reported in Chapter III on additives. Performance of this sample was comparable to the other samples in this group, i.e. significant power decline occurred only as a result of thermal shocks caused by power failures. The hot shoe remained intact on this sample although this joint failed on all the other elements in the test group which were bonded to iron shoes.

TABLE VIII

Torsion Strength of p-PbTe Bonded to Stainless Steel Shoes
(Room Temperature)

Element #	Torsion Strength, psi	Remarks
444	350	Broke in element, fracture not helical
457	650	Helical fracture in element starting at bond interface
523	700	Helical fracture in element near bond
524	650	Helical fracture in element near bond

However, the cold side bond separated on the stainless steel sample. Post-test measurements did not clearly indicate any difference in performance although there is an indication that low temperature Seebeck coefficient increased in the stainless steel shoe sample and decreased on those bonded to iron shoes. Two additional elements bonded to stainless steel shoes are currently under test, hence further data will be acquired.

The limited results obtained to date are not extremely promising. While the use of stainless steel shoes does minimize the internal stresses in p-PbTe, it does not appear to simplify bonding procedures nor is it likely to extend the life of bonded elements. While limited durther work in this area may be worthwhile, extensive development does not appear to be warranted at this time.

VI. <u>REFERENCES</u>

1. Abraham L. Eiss, <u>Thermoelectric Bonding Study, Phase II - Summary Report</u>, Report No. HIT-205 prepared under Contract NAS5-3973 by Hittman Associates (April 1966).

2. Personal communication from J. Mueller, BMI and M. Weinstein, Tyco Laboratories (August 1965).

3. Abraham L. Eiss, <u>Thermoelectric Bonding Study</u>, NASA-CR-369 (January 1966).

February 9, 1967

Refer to:
HA-7133

To: Distribution

From: A. L. Eiss, Hittman Associates, Inc.

Subject: Contract NAS5-3973
           Report HIT-237, Thermoelectric Bonding Study, Phase III -
           Summary Report

ERRATA NOTICE

On Figures 2 - 4 and 8 - 24, the unit for the ordinate on the lower curve
   should be changed from T, $^{\circ}$F to ΔT, $^{\circ}$F.

On Table III - page III-24, the correct title is:

       Properties of p-PbTe Thermoelectric Elements
             After 3576 Hour Life Test

Very truly yours,

HITTMAN ASSOCIATES, INC.

Abraham L. Eiss
Project Engineer

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